EXHIBIT V

PART 5

US005189106A

United States Patent [19]

Morimoto et al.

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[45] Date of Patent: Feb. 23, 1993

[54] POLYETHYLENE COMPOSITION

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[21] Appl. No.: 814,774

[22] Filed: Dec. 30, 1991

[51] Int. Cl.[5] C08L 23/06; C08L 23/08; C08L 23/16

[52] U.S. Cl. 525/240; 525/53; 525/324; 525/320; 525/322; 525/222; 525/227

[58] Field of Search 525/240, 53, 324

[56] References Cited

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Primary Examiner—Carman J. Seccuro, Jr.
Attorney, Agent, or Firm—Yahwak & Associates

[57] ABSTRACT

A polyethylene composition which has excellent flow characteristics and mechanical properties, especially low temperature mechanical properties as well as thermal stability, elasticity and workability for molding. The polyethylene composition comprises 20 to 80 wt. % of an ethylene-α-olefin copolymer of higher molecular weight having (a) intrinsic viscosity (η_1) of 1.2 to 9.0 dl/g, (b) density (d_1) of 0.890 to 0.935 g/cm^3 (c) a specific areal ratio calculated with an elution temperature-eluate volume curve in elution fractionation, and (d) a specific quantity of the content which is soluble in 25° C. o-dichlorobenzene, and 80 to 20 wt. % of ethylene homopolymer or ethylene-α-olefin copolymer of lower molecular weight having (e) intrinsic viscosity (η_2) of 0.2 to 1.6 dl/g, (f) density (d_2) of 0.890 to 0.980 g/cm^3 and, wherein the above (η_1) is larger than (η_2), and the prepared composition has an intrinsic viscosity (η) of 0.77 to 5.2 dl/g, a density (d) of 0.890 to 0.950 g/cm^3 and a specific N-value of 1.7 to 3.5.

5 Claims, 8 Drawing Sheets

FIG. 1

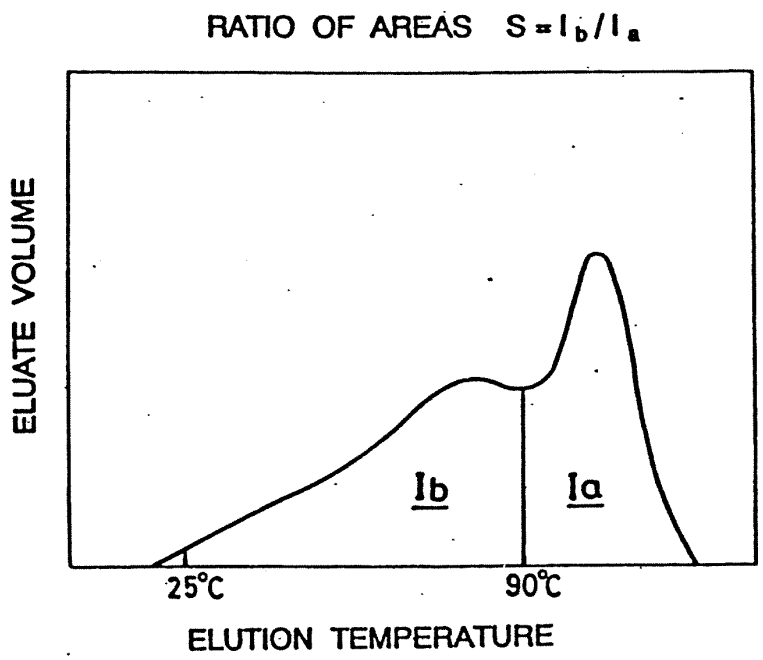

RATIO OF AREAS S = Ib/Ia
ELUATE VOLUME
Ib
Ia
25°C
90°C
ELUTION TEMPERATURE

FIG. 2

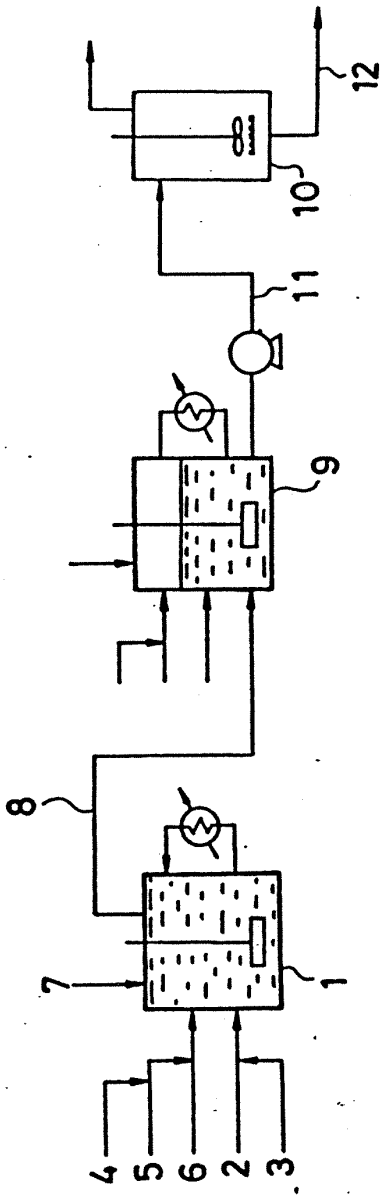


FIG. 3

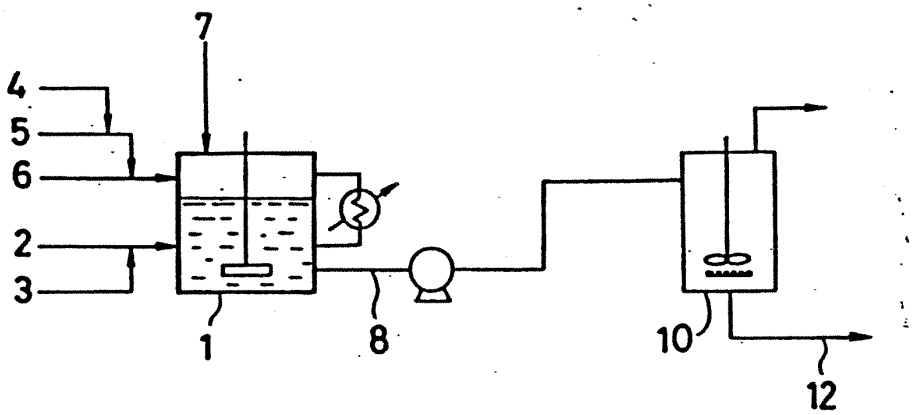


FIG. 4

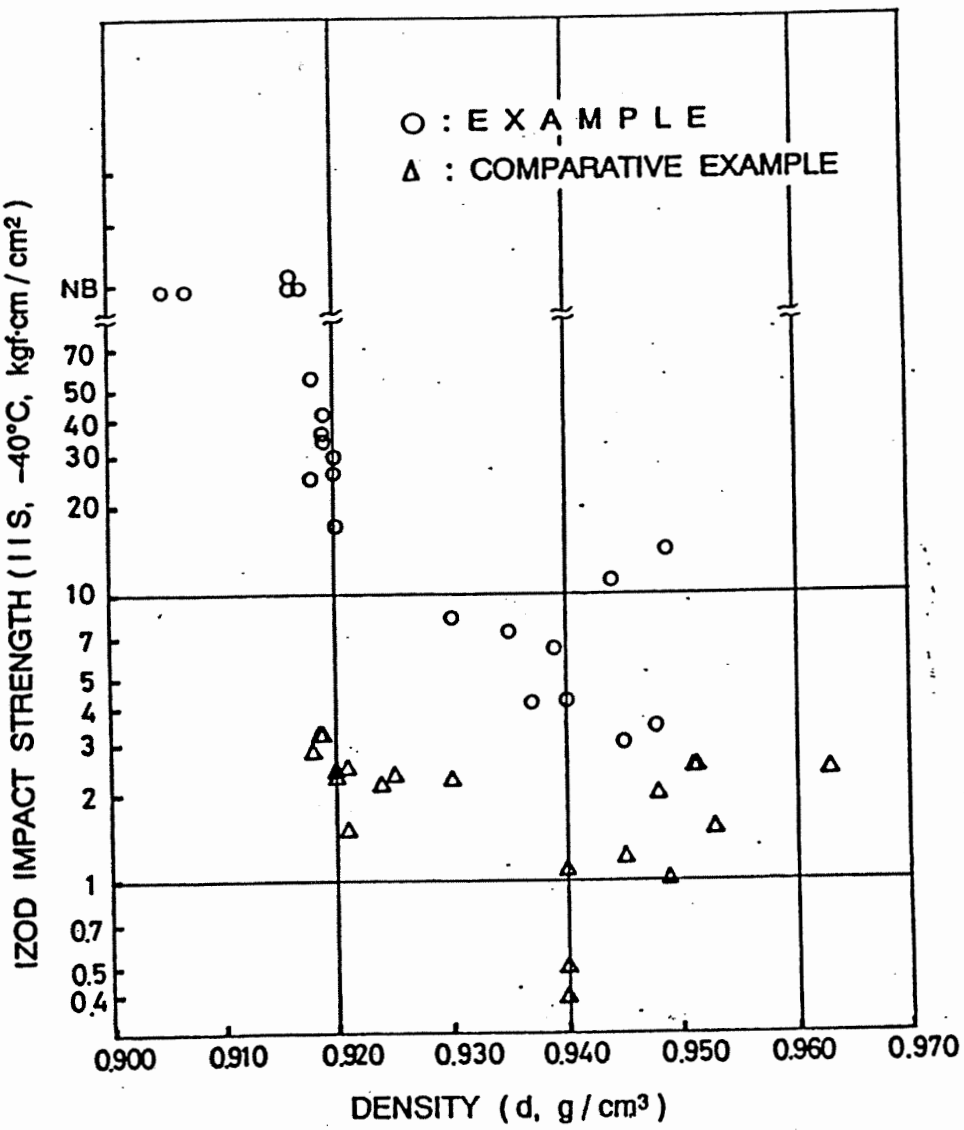

O : EXAMPLE
Δ : COMPARATIVE EXAMPLE
IZOD IMPACT STRENGTH (I I S, −40°C, kgf·cm / cm²)
NB
70
50
40
30
20
10
7
5
4
3
2
1
0.7
0.5
0.4
0.900
0.910
0.920
0.930
0.940
0.950
0.960
0.970
DENSITY (d, g / cm³)

FIG. 5

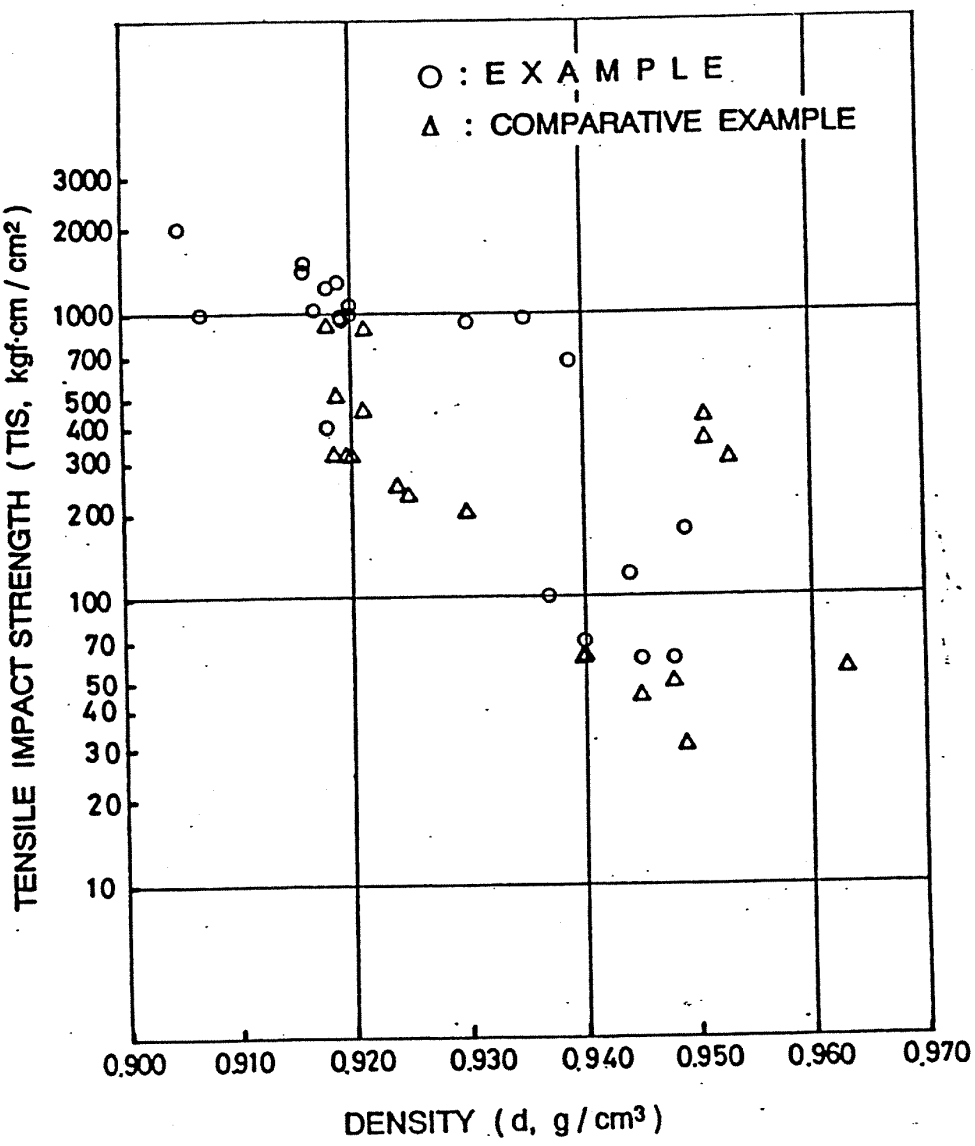

O : EXAMPLE
Δ : COMPARATIVE EXAMPLE
TENSILE IMPACT STRENGTH (TIS, kgf·cm/cm²)
3000
2000
1000
700
500
400
300
200
100
70
50
40
30
20
10
0.900
0.910
0.920
0.930
0.940
0.950
0.960
0.970
DENSITY (d, g/cm³)

FIG. 6

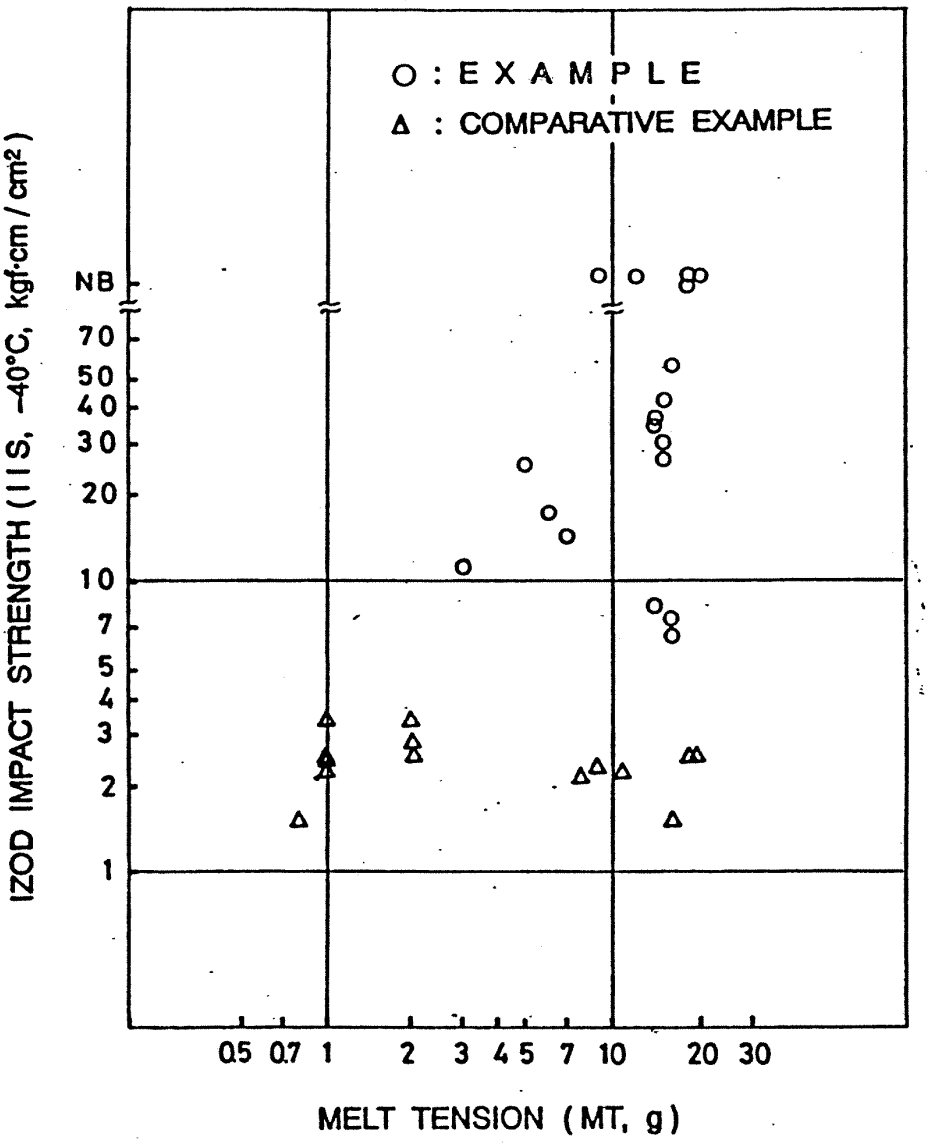

O : EXAMPLE
Δ : COMPARATIVE EXAMPLE
IZOD IMPACT STRENGTH (IIS, -40°C, kgf·cm/cm²)
NB
70
50
40
30
20
10
7
5
4
3
2
1
0.5 0.7 1 2 3 4 5 7 10 20 30
MELT TENSION (MT, g)

FIG. 7

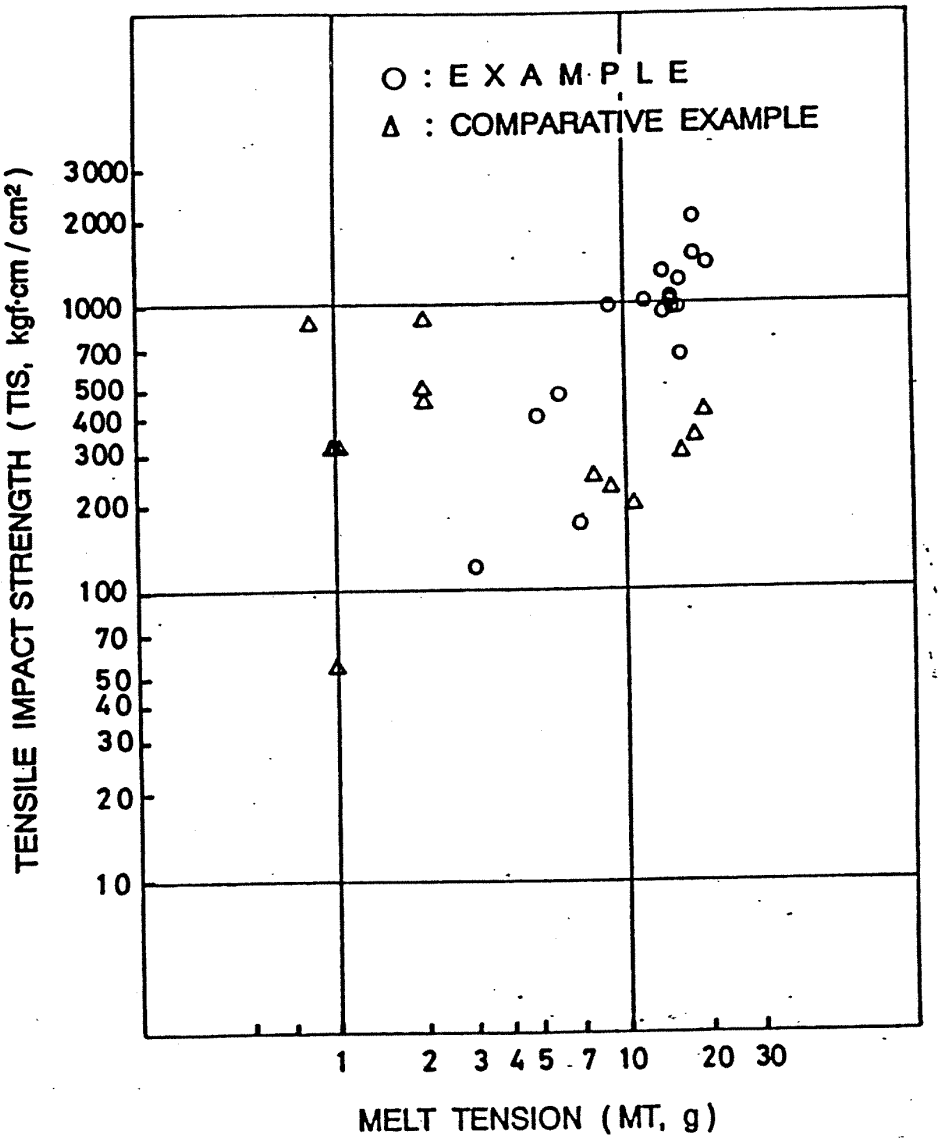
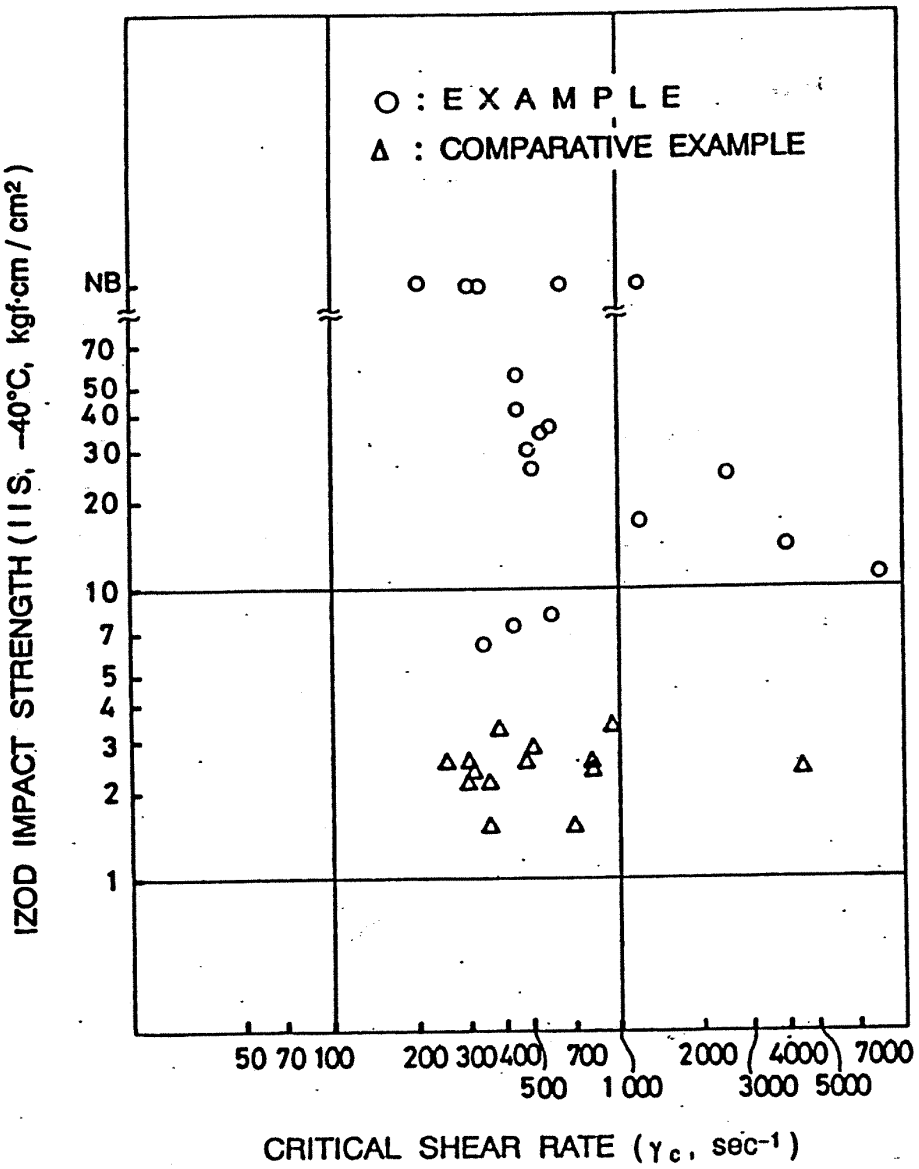

O : EXAMPLE
Δ : COMPARATIVE EXAMPLE
TENSILE IMPACT STRENGTH (TIS, kgf·cm/cm²)
3000
2000
1000
700
500
400
300
200
100
70
50
40
30
20
10
1
2
3
4
5
7
10
20
30
MELT TENSION (MT, g)

FIG. 8


○ : EXAMPLE
△ : COMPARATIVE EXAMPLE
IZOD IMPACT STRENGTH (IIS, −40°C, kgf·cm / cm²)
NB
70
50
40
30
20
10
7
5
4
3
2
1
50 70 100
200 300 400 500 700 1 000
2000 3000 4000 5000 7000
CRITICAL SHEAR RATE (γc, sec⁻¹)

POLYETHYLENE COMPOSITION

BACKGROUND OF THE INVENTION

(1) Field of the Invention

The present invention relates to a novel polyethylene composition. More particularly, the invention relates to a polyethylene composition which has a wide molecular weight distribution, good fluidity and excellent mechanical properties at low temperatures. Furthermore, the polyethylene composition of the invention comprises a high molecular weight ethylene-α-olefin copolymer having a very wide distribution of short branched chains among molecules and a relatively low molecular weight ethylene homopolymer or ethyl-α-olefin copolymer, which composition excels in melt elasticity, flow characteristics and mechanical properties, especially in low temperature conditions.

(2) Description of the Prior Art

The conventional high-pressure low density polyethylene (HP-LDPE) is prepared by radically polymerizing ethylene at high pressures and high temperatures in tubular reactors or autoclaves. This HP-LDPE has long branched chains which are equal to the length of main chains and short branched chains of alkyl groups having 1 to 6 carbon atoms. Accordingly, the HP-LDPE is soft and low in crystallinity. For this reason, the HP-LDPE is worse in mechanical properties such as environmental stress cracking resistance, tensile impact value, dart impact value and tear strength. It is inferior in the mechanical strength especially at low temperatures.

On the other hand, the linear low density polyethylene (LLDPE) is an ethylene-α-olefin copolymer which is produced under various polymerization conditions with various catalysts through several processes such as gas phase polymerization, slurry polymerization, solution polymerization and high pressure ion polymerization. The mechanical properties of LLDPE is superior to those of HP-LDPE because the former LLDPE has only short branched chains which depend upon the kind of used α-olefin.

However, because the molecular weight distribution of LLDPE is generally very narrow, it is worse in melt elasticity such as melt tension and flow characteristics such as N-value, flow parameter and critical shear velocity. The defects in the melt elasticity and flow characteristics have influences on workability in forming process. More particularly, there are several problems in the forming process concerning the smaller extrusion quantity, higher extrusion pressure, larger electric power consumption, insufficient high speed forming property, occurrence of fish eyes, roughness in the surfaces of formed products, and thermal deterioration caused by the excess heat generation in extruders.

When the molecular weight is made low in order to improve the flow characteristics of LLDPE, there occurs several defects in the lowering of mechanical properties such as impact strength and environmental stress cracking resistance, especially in the lowering of low temperature mechanical strength and melt elasticity. Furthermore, when the density is made lower for the purpose of improving mechanical properties, the melt elasticity can hardly be improved.

As described above, it has been quite difficult to improve the mechanical properties, especially low temperature mechanical properties, and flow characteristics and melt elasticity, simultaneously.

In the conventional art, there are proposed some methods to widen the molecular weight distribution of ethylene-α-olefin copolymer in order to improve the flow characteristics (e.g. Japanese Laid-Open Patent Publication No. Sho 57-21409 and Japanese Patent Publication No. Sho 63-47741). Even when the molecular weight distribution is widened like the proposed methods, however, the melt elasticity and mechanical properties, especially low temperature mechanical properties, cannot be improved but they are made worse seriously.

Furthermore, concerning the improvement in mechanical properties and flow characteristics in an ethylene-α-olefin copolymer which is composed of high molecular weight components and low molecular weight components, it was tried to improve not only the mechanical properties and flow characteristics but also the environmental stress cracking resistance (ESCR) by specifying the degree of short chain branching in high molecular weight components and by introducing a large quantity of short branched chains into the high molecular weight components (Japanese Laid-Open Patent Publication No. Sho 54-100444 and Japanese Patent Publication No. Sho 64-7096). The improvement to some extent can be attained in the above methods because the mechanical properties, especially the low temperature mechanical properties, are largely dependent upon the distribution of short branched chains in high molecular weight components. The methods are, however, still unsatisfactory in view of the measure to improve the mechanical properties and flow characteristics, especially those in low temperature conditions.

BRIEF SUMMARY OF THE INVENTION

In view of the state of the art mentioned above, it is the principal aspect of the present invention to provide a polyethylene composition which is excellent in melt elasticity, flow characteristics and mechanical properties, especially low temperature mechanical properties, which problems have never been solved in the conventional art.

Pursuant to the above aspect the inventors of the present invention have carried out extensive investigations, and as a result, a polyethylene composition which meets the requirement in melt elasticity, flow characteristics and mechanical properties, especially low temperature mechanical properties was produced thereby accomplishing the present invention.

According to the present invention, the novel polyethylene composition comprises:

(I) 20 to 80 wt. % of a copolymer of ethylene and α-olefins having 3 to 18 carbon atoms, which copolymer meets the following conditions (a) to (d):

(a) intrinsic viscosity (η_1) 1.2 to 9.0 dl/g

(b) density (d_1): 0.890 to 0.935 g/cm^3

(c) in the elution temperature-eluate volume curve in continuously temperature rising elution fractionation, the ratio S (Ib/Ia) of the area Ib under the curve of elution temperature of 25° to 90° C. to the area Ia under the curve of elution temperature of 90° C. and above, is not larger than the value S_1 which is calculated with the following equation,

$$S_1 = \eta_1^{-1} \exp\left[-50(d_1 - 0.900)\right]$$

(d) the quantity W wt. % of the content which is soluble in 25° C. o-dichlorobenzene is not

smaller than the the value W_1 which is calculated with the following equation,

$$W_1 = 20 \exp(-\eta_1)$$

and

(II) 80 to 20 wt. % of ethylene homopolymer and/or the copolymer of ethylene and α-olefins having 3 to 18 carbon atoms, which meet the following conditions (e) and (f),

(e) intrinsic viscosity (η_2): 0.2 to 1.6 dl/g

(f) density (d_2): 0.890 to 0.980 g/cm³

the value (η_1) is larger than (η_2), and the intrinsic viscosity (η) of the composition is 0.77 to 5.2 dl/g, the density (d) thereof is 0.890 to 0.950 g/cm³ and the N-value calculated with the following equation is 1.7 to 3.5.

$$N\text{-Value} = \frac{\log(\dot{\gamma}_{150}/\dot{\gamma}_{20})}{\log(\tau_{150}/\tau_{20})}$$

wherein "$\dot{\gamma}$" is an apparent shear rate (sec^{-1} at 170° C.) and "τ" is an apparent shear stress (dyne/cm² at 170° C.) and the subscripts "20" and "150" indicate loads of 20 kg/cm² and 150 kg/cm², respectively.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other desirable aspects and features of the invention will become more apparent from the following description taken in connection with the accompanying drawings, in which

FIG. 1 is a graph showing an elution temperature-eluate volume curve in continuous temperature rising fractionation (TREF) method to obtain an areal ratio S;

FIG. 2 is a flow sheet of two-step polymerization process used in the examples of the present invention;

FIG. 3 is a flow sheet of one-step polymerization process used in the examples of the present invention;

FIG. 4 is a graph showing the relation between densitity and Izod impact strength (−40° C.);

FIG. 5 is a graph showing the relation between densitity and tensile impact strength;

FIG. 6 is a graph showing the relation between melt tension and Izod, impact strength (−40° C.);

FIG. 7 is a graph showing the relation between melt tension and tensile impact strength; and

FIG. 8 is a graph showing the relation between critical shear rate and Izod impact strength (−40° C.).

DETAILED DESCRIPTION OF THE INVENTION

In the following, the present invention will be described in more detail with reference to several examples.

The ethylene-α-olefin copolymer as the higher molecular weight component (I) in the present invention comprises the copolymer of ethylene and α-olefins having 3 to 18 carbon atoms. The α-olefins having 4 to 10 carbon atoms are preferable in view of mechanical properties. More particularly, the α-olefin is exemplified by 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene and 1-decene. These α-olefins can be used as a mixture of two or more kinds.

The (a) intrinsic viscosity (η_1) of the ethylene; α-olefin copolymer as the higher molecular weight component (I) is in the range of 1.2 to 9.0 dl/g, preferably 1.4 to 8.5 dl/g, and more preferably 1.6 to 8.0 dl/g. When the value η_1 is smaller than 1.2 dl/g, the melt elasticity and mechanical properties are worse. On the other hand, when the value η_1 is larger than 9.0 dl/g, the workability is worse with the occurrence of surface roughening and fish eyes.

The (b) density (d_1) of the component (I) is in the range of 0.890 to 0.935 g/cm³, preferably 0.890 to 0.930 g/cm³. When the density (d_1) is lower than 0.890 g/cm³, it is undesirable because the forming operation is difficult and the composition is tacky. On the other hand, when the (d_1) is higher than 0.935 g/cm³, the melt elasticity and mechanical properties are undesirably worse.

As mentioned in the foregoing item (c), the distribution of branched chain in the composition (I) is measured in view of the dissolving temperature in a solvent according to Temperature Rising Elution Fractionation (TREF) of L. Wild et al. (Journal of Polymer Science, Polymer Physics Edition, Vol. 20, 441–455 (1982)). It is necessary that, in the elution temperature-eluate volume curve in TREF method, the area Ib under the curve of elution temperature of 25° to 90° C. and the area Ia under the curve of elution temperature above 90° C. must have a specific relationship. That is, the areal ratio (S=Ib/Ia) in the schematically illustrated FIG. 1 must not exceed the value S_1 which is calculated with the following equation.

$$S_1 = 20\,\eta_1^{-1} \exp[-50(d_1 - 0.900)]$$

When the value S exceeds the value S_1, it is not desirable in that the distribution of branched chains become almost even resulting in the decrease of highly branched components which is quite effective to improve the melt elasticity and mechanical properties, especially low temperature mechanical properties.

In the component (I) of the present invention, the content (d) which is soluble in 25° C. o-dichlorobenzene (ODCB) indicates the quantity of component which contains branched chains of a very large quantity to the extent that it cannot be determined by the continuously temperature rising elution fractionation because the elution temperature is too low. This value must be larger than a certain value. That is, it is necessary that the quantity of soluble content W wt. % is not smaller than the value W_1, preferably larger than W_2 which are calculated with the following equations:

$$W_1 = 20 \exp(-\eta_1)$$

$$W_2 = 22 \exp(-\eta_2)$$

When the value (W) is smaller than W_1, it is not desirable as described above because the quantity of highly branched component which is largely effective to the melt elasticity and mechanical properties, especially low temperature mechanical properties, is small.

The lower molecular weight component (II) of the present invention is ethylene homopolymer or the copolymer of ethylene and α-olefins. In the like manner as the component (I), the α-olefin for preparing the ethylene-α-olefin is those having 3 to 18 carbon atoms, preferably 4 to 10 carbon atoms. In view of mechanical properties, preferable α-olefins are exemplified by 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene and 1-decene. These α-olefins can also be used as a mixture of two or more kinds.

The value (e) of intrinsic viscosity (η)of the above component (II) is in the range of 0.2 to 1.6 dl/g, prefera-

bly 0.3 to 1.5 dl/g and more preferably 0.4 to 1.4 dl/g. When the value η is lower than 0.2 dl/g, the mechanical properties, especially low temperature mechanical properties of the obtained composition are worse. On the other hand, when it exceeds 1.6 dl/g, the flow characteristics are low, which is not desirable either.

The value (f) of density (d_2) of the component (II) is in the range of 0.890 to 0.980 g/cm^3, preferably 0.900 to 0.976 g/cm^3. When d_2 is smaller than 0.890 g/cm^3, it is not desirable because the plastics forming operation is difficult and the composition is tacky. On the other hand, when the density (d_2) is higher than 0.980 g/cm^3, not only the forming operation is difficult but also the mechanical properties of the composition is not good.

The compounding ratios of both the components in the present invention are 20 to 80 wt. % of component (I) and 80 to 20 wt. % of component (II), preferably 30 to 70 wt. % and 70 to 30 wt. %, respectively. When the quantity of component (I) is smaller than 20 wt. %, the melt elasticity and mechanical properties, especially low temperature mechanical properties, are worse. Meanwhile, when the quantity of component (II) is larger than 80 wt. %, the flow characteristics is worse. Accordingly, the compositions in both the outside of the above range cannot be used.

When the component (I) and component (II) are mixed together, it is necessary that the intrinsic viscosity of the component (I) is larger than that of the component (II). If the components do not meet this condition, it is difficult to attain the object of the present invention to improve the mechanical properties at low temperatures.

As described above, the composition of the present invention can be prepared by mixing both the components (I) and (II), in which the properties of the composition after mixing must meet specific ranges. That is, the intrinsic viscosity (η) of the polyethylene composition must be in the range of 0.77 to 5.2 dl/g, preferably 1 to 4 dl/g. When the value (η) is lower than 0.77 dl/g, the melt viscosity and mechanical properties, especially low temperature mechanical properties are worse and when it exceeds 5.2 dl/g, flow characteristics are low, both of which are not desirable.

The density (d) of the polyethylene composition is in the range of 0.890 to 0.950 g/cm^3, preferably 0.900 to 0.940 g/cm^3. When the density (d) is lower than 0.890 g/cm^3, it is not desirable because the forming operation is difficult and the composition is tacky. On the other hand, when the density (d) is higher than 0.950 g/cm^3, mechanical properties such as tensile impact strength is low.

It is necessary that the N-value of polyethylene composition is in the range of 1.7 to 3.5, preferably 1.7 to 3.0. When the N-value is lower than 1.7, the high speed forming is difficult. When the N-value is higher than 3.5, melt fracture is liable to occur.

The method to formulate the polyethylene composition of the present invention is not especially limited. For example, the component (I) and the component (II) are prepared separately through one-step polymerization process and they are then mixed together by a conventional method. The polyethylene composition may also be prepared by the conventionally known two-step polymerization process or by multi-step polymerization process.

In the former preparation by mixing, any known method can be adopted by using a uniaxial extruder, biaxial extruder or Banbury mixer or by solution mixing method.

In the above-mentioned multi-step polymerization method, a plurality of reactors are used. For example, a first reactor is set to the polymerization conditions for the higher molecular weight ethylene-α-olefin of the component (I) and a second reactor is set to the polymerization conditions for the lower molecular weight polymer of the component (II). The polymerization product from the first reactor is continuously passed into the second reactor to obtain the polyethylene composition of the present invention. In this procedure, each component (I) or (II) may be prepared in any of reactors. That is, preparation can be carried out in arbitrary order and number of steps.

In the above process, the type of reaction is not limited, for example, any of slurry method, gas phase method, solution method and high pressure ionic method can be employed. The polymerization catalyst is not limited either. For example, any of Ziegler catalyst, Phillips catalyst and Kaminsky catalyst can be used. Among several catalysts, a most desirable one is highly active Ziegler catalyst being carried on a solid carrier, which will be described in more detail.

The highly active Ziegler catalyst comprises a solid component of transition metal compound which is carried on an inorganic solid carrier. The inorganic solid carriers are exemplified by metallic magnesium, magnesium hydroxide, magnesium carbonate, magnesium oxide, magnesium chloride, several kinds of alumina, silica, and silica-alumina, or double salts or double oxides, hydrates of carbonates and hydrates of silicates containing magnesium and one member selected from the group consisting of silicon, aluminum and calcium, and the substances which are prepared by treating or reacting these inorganic solid carriers with oxygen-containing compounds, sulfur-containing compounds, hydrocarbons or halogen-containing compounds. The transition metal compounds are exemplified by halides, alkoxyhalides, oxides and halogenated oxides of transition metals such as titanium, vanadium, zirconium and chromium, or combinations of these compounds with organometallic compounds of metals of Group I to IV of the periodic table, and preferably organo-zinc compounds or organo-aluminum compounds, or the substances which are prepared by pretreating the above exemplified materials with α-olefins. The catalytic activity is generally more than 50 g-polymer/g-catalyst.hr.kg/cm^2-olefin pressure, preferably more than 100 g-polymer/g-catalyst.hr.kg/cm^2-olefin pressure.

Within the scope of the present invention, any conventionally know additive can be incorporated into the polyethylene composition. The additives are exemplified by other olefinic polymers such as high, medium and low density polyethylene, ethylene-vinyl acetate copolymer, ethylene-ethylacrylate copolymer, ethylene-ethylmethacrylate copolymer and polypropylene, rubber, antioxidant, UV absorber, light stabilizer, lubricant, antistatic agent, antiblocking agent, processing aid and coloring pigment.

In the following, the present invention will be described in more detail with reference to several examples. The preferred embodiments described herein are illustrative and not restrictive, the scope of the invention being indicated by the appended claims and all variations which come within the meaning of the claim are intended to be embraced therein.

In the first place, the test methods employed herein are described.

(1) Intrinsic viscosity

The value of (η) was measured in 135° C. decalin solution.

(2) Density

Measured by density gradation tube method at 23° C. according to JIS K 6760.

(3) Continuously temperature rising fractionation method (TREF)

Measured according to L. Wild's method as mentioned in the foregoing paragraph.

(4) Ratio (S) of areas in TREF

Measured according to the foregoing paragraph with FIG. 1.

(5) Component (W) soluble in o-dichlorobenzene at 25° C.

A test sample (0.5 g) was heated for 2 hours in 20 ml of 135° C. o-dichlorobenzene (ODCB) to dissolve the sample completely, which was followed by cooling to 25° C. in 2 hours. This solution was left to stand still at 25° C. for one night and was filtered through a Teflon filter. The filtrate was analyzed by an infrared spectrometer to obtain the absorption at a wave number of 2,950 cm^{-1} corresponding to the asymmetrical vibration of methylene. The concentration in the sample was determined with an obtained result in comparison with a previously made calibration curve.

(6) N-value

Measured with a flowtester (Shimadzu Capillary Rheometer made by Shimadzu Corp., Ltd.) Test sample was extruded through a die of 2 mmϕ×40 mm at 170° C. for the material of MFR of 0.1 or higher and at 210° C. for the material of MFR of lower than 0.1 to obtain apparent shear rates at a low test pressure of 20 kg/cm^2 and a high test pressure of 150 kg/cm^2 and N-value was calculated with the following equation.

$$N\text{-Value} = \frac{\log(\dot{\gamma}_{150}/\dot{\gamma}_{20})}{\log(\tau_{150}/\tau_{20})}$$

wherein "$\dot{\gamma}$" is an apparent shear rate (sec^{-1} at 170° C.) and "τ" is an apparent shear stress (dyne/cm^2 at 170° C.) and the subscripts "20" and "150" indicates loads of 20 kg/cm^2 and 150 kg/cm^2, respectively.

(7) Melt flow rate (MFR)

Measured the value of MFR according to JIS K 6760 at 190° C. with 2.16 kg load.

(8) High load melt flow rate (HLMFR)

Measured the value of HLMFR according to JIS K 6760 at 190° C. with 2.16 kg load.

(9) Flow parameter

The value of FP was calculated with the following equation.

$$FP = \log(HLMFR/MFR)$$

(10) Yield tensile strength (YTS)

Measured according to JIS K 6760 at a tensile rate of 50 mm/min with test pieces of 2 mm in thickness.

(11) Tensile impact strength (TIS)

Measured according to ASTM D 1822 with test pieces of 2 mm in thickness.

(12) Izod Impact Strength (IIS)

Measured according to JIS K 7110 at 23° C. and −40° C. Sheets of 3 mm thick for measurement at 23° C. and of 4 mm thick for measurement at −40° C. were made from a test sample using a press. The size of test pieces was No. 2-A. The test pieces were conditioned at 23° C. and 50% humidity for 88 hours and were used for the tests at 23° C. and −40° C. Meanwhile, the test pieces for use in −40° C. test were further conditioned by placing them in an air bath at −40° C. for about 3 hours and were subjected to the test without delay. The number of test pieces were five and an average of five test results were taken, respectively.

(13) Flexural Strength

Measured according to JIS K 7106 using a flexural strength testing machine made by Toyo Seiki Seisaku-sho, Ltd.

(14) Melt tension (MT)

Measured at 190° C. using a melt tension tester made by Toyo Seiki Seisaku-sho, Ltd.

(15) Critical shear rate (γ_1)

Measured at 190° C. using a capillary rheometer made by International Technology & Science Corp.

(16) Melting point (T_m)

Measured by using a differentially scanning calorimeter made by Rigaku Corp. and the data indicated are the temperature of the maximum peak. Test pieces were made of pressed sheets of 0.2 mm thick.

(17) Spiral flow length

Test pieces were made by injection molding at an injection temperature of 230° C. and an injection pressure of 1,000 kg/cm^2 using a metal mold having a certain spiral cavity with an injection molding machine (IS 100 EN made by Toshiba Machine Co., Ltd.) The melt flow property was determined by measuring the lengths of molded spirals.

(18) Environmental stress cracking resistance (ESCR)

Measured according to JIS K 6760 and the value of F_{50} of constant strain ESCR was indicated.

EXAMPLE 1

A two-step polymerization process is shown in FIG. 2. A 30 liter reaction vessel equipped with a stirrer was used as a first step reactor 1. The used solid catalyst was titanium tetrachloride being supported on a solid carrier containing a component of anhydrous magnesium chloride. This catalyst was fed through a line 2 and a promoter of triethyl aluminum (TEA) was fed through a line 3. Starting materials of ethylene and 1-butene were continuously polymerized under the polymerization conditions shown in Table 1. In the drawing, the numeral 4 denotes an ethylene feeding line, 5 a 1-butene feeding line, 6 a hydrogen feeding line, and 7 a solvent feeding line. The polymerization conditions in the first step reactor 1 were 60° C. in temperature and 8.8 kg/cm^2G in total pressure and the inside of the reactor was filled with liquid. The quantity E_1 of polymerization product calculated from heat balance was 1.59 kg. A part of polymerization product was taken out from the first step reactor and properties of recovered polymer were analyzed, the results of which are shown in Table 5A.

The polymerization product in slurry from the first step reactor 1 was introduced into a 70 liter second step reactor 9 through a line 8. As shown in Table 1, ethylene, 1-butene and hydrogen were additionally fed and polymerization was continued at a polymerization temperature of 65° C., a total pressure of 8.6 kg/cm^2G and a liquid phase volume of 50 liter. The polymerization product taken out from the second reactor 9 was then introduced into a flashing vessel 10 through a line 11.

The polymerization product was recovered continuously from a line 12 and subjected to analysis, the results of which are shown in the following Table 5A.

The quantity E of the finally recovered polymerization product was 3.38 kg, which coincided with the calculated value of E_1+E_2. The average polymerization times of the first step reactor 1 and the second step reactor 9 were 25 minutes and 40 minutes, respectively.

EXAMPLES 2 TO 17 AND COMPARATIVE EXAMPLES 1 TO 6

In the like manner as in Example 1, two-step polymerization was carried out with changing the kind of α-olefin and polymerization conditions. The polymerization conditions are shown in Tables 1 to 4 and the results of property tests are shown in Table 5A to 8B.

TABLE 1

		Two Step Polymerization Conditions (1)					
		Examples					
Items	Units	1	2	3	4	5	6
First Step Polymerization (Higher Molecular Weight)							
Qty. of Solvent	l/hr	70	70	70	70	70	70
Qty. of Ethylene	kg/hr	1.7	2.0	1.7	1.7	2.2	2.0
Qty. of Comonomer	l/hr	1.7	6.7	2.0	2.9	4.9	2.7
Kind of Comonomer	—	C_4	C_4	C_4	C_6	C_6	C_4
Qty. of Hydrogen	Nl/hr	3.7	3.5	3.2	2.7	4.0	4.1
Qty. of Solid Catalyst	g/hr	0.9	1.2	1.2	1.2	1.2	0.9
Qty. of Promoter (TEA)	mmol/hr	21	21	21	21	21	21
Polymerization Temperature	°C.	60	60	60	65	60	60
Polymerization Pressure	kg/cm²G	8.8	7.4	8.7	9.3	10.8	8.4
Polymerization Time	min	25	25	25	25	25	25
Second Step Polymerization (Lower Molecular Weight)							
Additional Qty. of Ethylene	kg/hr	1.3	1.1	1.6	2.0	1.3	1.8
Additional Qty. of Comonomer	l/hr	1.8	0	19	0	2.3	2.3
Kind of Additional Comonomer	—	C_4	—	C_4	—	C_6	C_4
Additional Qty. of Hydrogen	Nl/hr	98	82	145	120	187	130
Ratio of Hydrogen/ethylene in Gas Phase Section	by mole	2.33	1.87	2.90	2.22	2.69	2.17
Ratio of Comonomer/Ethylene in Gas Phase Section	by mole	0.22	0.19	0.20	0.11	0.28	0.25
Polymerization Temperature	°C.	65	65	65	70	65	65
Polymerization Pressure	kg/cm²G	8.6	7.1	8.5	9.1	10.5	8.2
Polymerization Time	min	40	40	40	40	40	40

TABLE 2

		Two Step Polymerization Conditions (2)					
		Examples					
Items	Units	7	8	9	10	11	12
First Step Polymerization (Higher Molecular Weight)							
Qty. of Solvent	l/hr	70	70	70	70	70	70
Qty. of Ethylene	kg/hr	1.7	1.8	1.8	2.0	1.3	1.2
Qty. of Comonomer	l/hr	1.4	1.0	2.0	8.3	0.43	0.43
Kind of Comonomer	—	C_6	C_4	C_4	C_4	C_4	C_4
Qty. of Hydrogen	Nl/hr	2.6	3.8	4.4	3.6	13	14
Qty. of Solid Catalyst	g/hr	0.9	0.9	0.9	1.5	1.0	1.0
Qty. of Promoter (TEA)	mmol/hr	21	21	21	21	21	21
Polymerization Temperature	°C.	65	65	60	55	70	70
Polymerization Pressure	kg/cm²G	11.5	11.0	8.5	8.2	8.0	8.2
Polymerization Time	min	25	25	25	25	25	25
Second Step Polymerization (Lower Molecular Weight)							
Additional Qty. of Ethylene	kg/hr	1.9	1.9	1.3	1.8	2.8	2.8
Additional Qty. of Comonomer	l/hr	0	0	1.8	2.5	0	0
Kind of Additional Comonomer	—	—	—	C_4	C_4	—	—
Additional Qty. of Hydrogen	Nl/hr	130	195	103	113	138	130
Ratio of Hydrogen/ethylene in Gas Phase Section	by mole	2.08	2.10	2.50	2.40	1.48	1.41
Ratio of Comonomer/Ethylene in Gas Phase Section	by mole	0.086	0	0.21	0.34	0.028	0.020
Polymerization Temperature	°C.	70	70	70	60	80	80
Polymerization Pressure	kg/cm²G	11.2	10.7	8.3	8.0	7.8	8.0
Polymerization Time	min	40	40	40	40	40	40

TABLE 3

		Two Step Polymerization Conditions (3)				
		Examples				
Items	Units	13	14	15	16	17
First Step Polymerization						

TABLE 3-continued

Two Step Polymerization Conditions (3)						
		Examples				
Items	Units	13	14	15	16	17
(Higher Molecular Weight)						
Qty. of Solvent	l/hr	70	70	70	70	70
Qty. of Ethylene	kg/hr	1.3	1.3	1.2	1.0	1.0
Qty. of Comonomer	l/hr	0.90	2.8	1.2	0.52	0.51
Kind of Comonomer	—	C_6	C_4	C_4	C_4	C_4
Qty. of Hydrogen	Nl/hr	12	3.0	5.0	8.0	13
Qty. of Solid Catalyst	g/hr	1.0	0.45	0.45	0.9	0.75
Qty. of Promoter (TEA)	mmol/hr	21	21	21	21	21
Polymerization Temperature	°C.	70	60	60	70	70
Polymerization Pressure	kg/cm^{2}G	8.2	7.0	9.1	14.2	10.0
Polymerization Time	min	25	25	25	25	25
Second Step Polymerization (Lower Molecular Weight)						
Additional Qty. of Ethylene	kg/hr	2.8	2.7	1.9	2.8	1.8
Additional Qty. of Comonomer	l/hr	0	1.1	1.4	0	0
Kind of Additional Comonomer	—	—	C_4	C_4	—	—
Additional Qty. of Hydrogen	Nl/hr	136	50	105	160	95
Ratio of Hydrogen/ethylene in Gas Phase Section	by mole	1.45	0.75	2.32	1.21	1.41
Ratio of Comonomer/Ethylene in Gas Phase Section	by mole	0.027	0.10	0.20	0.034	0.043
Polymerization Temperature	°C.	80	70	70	80	80
Polymerization Pressure	kg/cm^{2}G	8.0	6.8	8.9	14.0	9.8
Polymerization Time	min	40	40	40	40	40

TABLE 4

Two Step Polymerization Conditions (4)							
		Comparative Examples					
Items	Units	1	2	3	4	5	6
First Step Polymerization (Higher Molecular Weight)							
Qty. of Solvent	l/hr	70	70	70	70	70	70
Qty. of Ethylene	kg/hr	2.2	2.2	2.2	2.3	2.3	2.3
Qty. of Comonomer	l/hr	0.12	0.14	0.15	0.13	0.13	0.15
Kind of Comonomer	—	C_4	C_4	C_6	C_4	C_4	C_4
Qty. of Hydrogen	Nl/hr	18.8	20.5	20.4	6.3	7.3	7.3
Qty. of Solid Catalyst	g/hr	0.9	0.9	0.9	0.9	0.9	0.9
Qty. of Promoter (TEA)	mmol/hr	21	21	21	42	42	42
Polymerization Temperature	°C.	60	60	60	70	70	70
Polymerization Pressure	kg/cm^{2}G	12.0	11.9	11.6	12.4	12.9	12.1
Polymerization Time	min	25	25	25	25	25	25
Second Step Polymerization (Lower Molecular Weight)							
Additional Qty. of Ethylene	kg/hr	1.1	1.1	1.0	1.3	1.3	1.3
Additional Qty. of Comonomer	l/hr	4.5	5.2	6.4	0	0	0
Kind of Additional Comonomer	—	C_4	C_4	C_6	—	—	—
Additional Qty. of Hydrogen	Nl/hr	238	220	172	273	244	239
Ratio of Hydrogen/ethylene in Gas Phase Section	by mole	2.19	2.20	2.20	2.18	2.43	2.50
Ratio of Comonomer/Ethylene in Gas Phase Section	by mole	0.20	0.24	0.34	0	0	0
Polymerization Temperature	°C.	65	65	65	80	80	80
Polymerization Pressure	kg/cm^{2}G	11.8	11.6	11.3	12.1	12.5	11.8
Polymerization Time	min	40	40	40	40	40	40

TABLE 5A

Physical Properties in Two-Step Polymerization (1A)								
			Examples					
Items		Units	1	2	3	4	5	6
(Higher Molecular Weight Components A)								
Intrinsic Viscosity	η_1	dl/g	4.3	4.6	5.4	5.3	5.9	5.0
Density	d_1	g/cm^3	0.916	0.904	0.913	0.909	0.910	0.913
Qty. Prepared	E_1	kg/hr	1.59	2.04	1.71	1.71	1.95	2.26
Percentage	X_1	wt. %	47	56	45	41	51	49
Ratio of Areas with TREF	S	—	1.0	3.0	1.4	1.9	1.3	1.4
Qty. soluble in 25° C. ODCB	W	wt. %	2.6	17.8	4.7	9.8	6.4	4.8
S_1		—	2.09	3.6	1.9	2.4	2.1	2.1
W_1		wt. %	0.27	0.20	0.09	0.10	0.05	0.13
(Lower Molecular Weight Components B)								

TABLE 5A-continued

Physical Properties in Two-Step Polymerization (1A)

Items		Units	Examples 1	2	3	4	5	6
Intrinsic Viscosity	η_2	dl/g	0.83	0.54	0.36	0.61	0.38	0.45
Density	d_2	g/cm^3	0.917	0.931	0.926	0.945	0.922	0.923
Qty. Prepared	E_2	kg/hr	1.79	1.60	2.12	2.45	1.88	2.33
Percentage	X_2	wt. %	53	44	55	59	49	51

TABLE 5B

Physical Properties in Two-Step Polymerization (1B)

Items		Units	Examples 1	2	3	4	5	6
(Polyethylene Composition)								
Qty. Prepared	E	kg/hr	3.38	3.64	3.38	4.16	3.83	4.59
Intrinsic Viscosity	η	dl/g	2.46	2.81	2.63	2.53	3.20	2.68
Melt Flow Rate	MFR	g/10 min	0.11	0.048	0.073	0.092	0.022	0.065
Density	d	g/cm^3	0.917	0.916	0.920	0.930	0.916	0.918
N-Value		—	2.45	2.52	2.82	2.68	2.87	2.63
Flow Parameter	FP	—	2.02	2.05	2.13	2.19	2.31	2.08
HLMFR/MFR		—	105	112	135	155	204	120
Yield Tensile Strength	YTS	kgf/cm^2	110	100	110	150	100	110
Tensile Impact Strength	TIS	kgf - cm/cm^2	1010	1480	1010	920	1380	1210
Izod Impact Strength	IIS							
(23° C., 3 mm)		kgf - cm/cm^2	NB*	NB	NB	NB	NB	NB
(−40° C., 4 mm)		kgf - cm/cm^2	NB	NB	30	8.1	NB	55
Flexural Strength (Olsen)		kgf/cm^2	1870	1780	2050	2780	1810	1860
Melt Tension	MT	g	12	18	15	14	20	16
Critical Shear Rate	γ_c	sec^{-1}	640	330	480	590	200	440
Melting Point	T_m	°C.	123	122	123	124	122	123
ESCR (Constant Strain)	F_{50}	hr	>1000	>1000	>1000	>1000	>1000	>1000
Spiral Flow Length		mm	—	—	—	—	—	—

NB*: Not broken

TABLE 6A

Physical Properties in Two-Step Polymerization (2A)

Items		Units	Examples 7	8	9	10	11	12
(Higher Molecular Weight Components A)								
Intrinsic Viscosity	η_1	dl/g	5.5	5.1	5.0	5.0	2.2	2.3
Density	d_1	g/cm^3	0.915	0.920	0.920	0.900	0.929	0.929
Qty. Prepared	E_1	kg/hr	1.66	1.70	1.54	1.68	1.08	1.03
Percentage	X_1	wt. %	42	44	45	50	27	26
Ratio of Areas with TREF	S	—	1.1	0.7	0.8	3.7	1.4	1.4
Qty. soluble in 25° C. ODCB	W	wt. %	3.2	1.3	1.8	36.0	4.0	3.7
S_1		—	1.7	1.4	1.47	4.00	2.1	2.0
W_1		wt. %	0.09	0.12	0.13	0.13	2.2	2.0
(Lower Molecular Weight Components B)								
Intrinsic Viscosity	η_2	dl/g	0.66	0.67	0.74	0.82	0.78	0.84
Density	d_2	g/cm^3	0.949	0.953	0.919	0.910	0.951	0.955
Qty. Prepared	E_2	kg/hr	2.34	2.16	1.88	1.68	2.93	2.87
Percentage	X_2	wt. %	54	56	55	50	73	74

TABLE 6B

Physical Properties in Two-Step Polymerization (2B)

Items (Polyethylene Composition)		Units	Examples 7	8	9	10	11	12
Qty. Prepared	E	kg/hr	4.00	3.86	3.42	3.36	4.01	3.90
Intrinsic Viscosity	η	dl/g	2.69	2.62	2.66	2.91	1.16	1.22
Melt Flow Rate	MFR	g/10 min	0.063	0.075	0.068	0.039	10	7
Density	d	g/cm^3	0.935	0.939	0.919	0.905	0.945	0.948
N-Value		—	2.66	2.52	2.43	2.41	1.80	1.79
Flow Parameter	FP	—	2.11	2.11	2.03	2.02	—	1.62
HLMFR/MFR		—	129	130	107	105	—	42
Yield Tensile Strength	YTS	kgf/cm^2	160	200	100	60	200	240
Tensile Impact Strength	TIS	kgf.cm/cm^2	960	660	960	2000	60	60
Izod Impact Strength	IIS							
(23° C., 3 mm)		kgf.cm/cm^2	NB	50	NB	NB	6	6
(−40° C., 4 mm)		kgf.cm/cm^2	7.3	6.4	42	NB	3.0	3.4
Flexural Strength (Olsen)		kgf/cm^2	3350	5000	2000	1000	5800	6200

TABLE 6B-continued

Physical Properties in Two-Step Polymerization (2B)

Items (Polyethylene Composition)		Units	Examples 7	8	9	10	11	12
Melt Tension	MT	g	16	16	15	18	—	—
Critical Shear Rate	γ_c	sec^{-1}	430	340	440	300	—	—
Melting Point	T_m	°C.	125	126	120	120	128	128
ESCR (Constant Strain)	F_{50}	hr	>1000	>1000	>1000	>1000	60	70
Spiral Flow Length		mm	—	—	—	—	600	530

TABLE 7A

Physical Properties in Two-Step Polymerization (3A)

Items		Units	Examples 13	14	15	16	17
(Higher Molecular Weight Components A)							
Intrinsic Viscosity	η_1	dl/g	2.5	4.3	3.8	5.0	3.1
Density	d_1	g/cm^3	0.918	0.910	0.909	0.927	0.930
Qty. Prepared	E_1	kg/hr	1.12	1.26	1.26	0.68	0.71
Percentage	X_1	wt. %	30	27	36	21	30
Ratio of Areas with TREF	S	—	2.4	2.1	2.7	0.5	0.9
Qty. soluble in 25° C. ODCB	W	wt. %	9.1	10.7	14.4	0.7	1.8
S_1		—	3.3	2.82	3.36	1.04	1.44
W_1		wt. %	1.6	0.27	0.45	0.13	0.90
(Lower Molecular Weight Components B)							
Intrinsic Viscosity	η_2	dl/g	0.80	1.05	0.66	1.00	0.93
Density	d_2	g/cm^3	0.945	0.926	0.924	0.955	0.950
Qty. Prepared	E_2	kg/hr	2.61	3.36	2.26	2.50	1.69
Percentage	X_2	wt. %	70	73	64	79	70

TABLE 7B

Physical Properties in Two-Step Polymerization (3B)

Items (Polyethylene Composition)		Units	Examples 13	14	15	16	17
Qty. Prepared	E	kg/hr	3.73	4.62	3.52	3.18	2.40
Intrinsic Viscosity	η	dl/g	1.31	1.93	1.80	1.84	1.58
Melt Flow Rate	MFR	g/10 min	5	0.50	0.79	0.68	1.7
Density	d	g/cm^3	0.937	0.920	0.918	0.949	0.944
N-Value		—	1.83	2.13	2.66	2.28	1.87
Flow Parameter	FP	—	1.60	1.92	2.24	2.06	1.78
HLMFR/MFR		—	40	83	174	115	60
Yield Tensile Strength	TYS	kgf/cm^2	190	120	105	280	240
Tensile Impact Strength	TIS	$kgf.cm/cm^2$	100	480	400	170	120
Izod Impact Strength	IIS						
(23° C., 3 mm)		$kgf.cm/cm^2$	8	NB	NB	40	16
(−40° C., 4 mm)		$kgf.cm/cm^2$	4.1	17	25	14	11
Flexural Strength (Olsen)		kgf/cm^2	4700	2100	2100	7400	5500
Melt Tension	MT	g	—	6	5	7	3
Critical Shear Rate	γ_c	sec^{-1}	—	1200	2500	4000	8400
Melting Point	T_m	°C.	126	123	122	128	127
ESCR (Constant Strain)	F_{50}	hr	130	>1000	>1000	90	50
Spiral Flow Length		mm	460	320	480	340	350

TABLE 8A

Physical Properties in Two-Step Polymerization (4A)

Items		Units	Comparative Example 1	2	3	4	5	6
(Higher Molecular Weight Components A)								
Intrinsic Viscosity	η_1	dl/g	5.0	5.0	4.9	5.2	5.0	4.9
Density	d_1	g/cm^3	0.934	0.938	0.933	0.931	0.932	0.933
Qty. Prepared	E_1	kg/hr	1.30	1.42	1.40	1.72	1.80	1.80
Percentage	X_1	wt. %	45	47	49	50	49	47
Ratio of Areas with TREF	S	—	0.17	0.15	0.24	0.29	0.30	0.29
Qty. soluble in 25° C. ODCB	W	wt. %	0.05	0.04	0.06	0.29	0.29	0.27
S_1		—	0.73	0.60	0.78	0.82	0.81	0.78
W_1		wt. %	0.13	0.13	0.15	0.11	0.13	0.15
(Lower Molecular Weight Components B)								
Intrinsic Viscosity	η_2	dl/g	0.49	0.53	0.47	0.54	0.53	0.50
Density	d_2	g/cm^3	0.927	0.913	0.915	0.970	0.970	0.971

TABLE 8A-continued

Physical Properties in Two-Step Polymerization (4A)								
			Comparative Example					
Items		Units	1	2	3	4	5	6
Qty. Prepared	E_2	kg/hr	1.58	1.58	1.47	1.72	1.88	2.03
Percentage	X_2	wt. %	55	53	51	50	51	53

TABLE 8B

Physical Properties in Two-Step Polymerization (4B)								
(Polyethylene			Comparative Example					
Composition)		Units	1	2	3	4	5	6
Qty. Prepared	E	kg/hr	2.88	3.00	2.87	3.44	3.68	3.83
Intrinsic Viscosity	η	dl/g	2.52	2.63	2.64	2.87	2.72	2.57
Melt Flow Rate	MFR	g/10 min	0.095	0.075	0.071	0.042	0.059	0.084
Density	d	g/cm^3	0.930	0.925	0.924	0.951	0.951	0.953
N-Value		—	2.58	2.47	2.48	2.65	2.59	2.63
Flow Parameter	FP	—	2.19	2.11	2.14	2.37	2.37	2.42
HLMFR/MFR		—	154	129	138	234	232	263
Yield Tensile Strength	YTS	kgf/cm^2	140	130	120	250	250	260
Tensile Impact Strength	TIS	kgf.cm/cm^2	200	230	250	430	350	300
Izod Impact Strength	IIS							
(23° C., 3 mm)		kgf.cm/cm^2	30	33	35	17	16	14
(−40° C., 4 mm)		kgf.cm/cm^2	2.2	2.3	2.1	2.5	2.5	1.5
Flexural Strength (Olsen)		kgf/cm^2	3700	3000	2900	7300	7300	7800
Melt Tension	MT	g	11	9	8	19	18	16
Critical Shear Rate	γ_c	sec^{-1}	350	310	300	250	300	350
Melting Point	T_m	°C.	126	125	125	128	128	129
ESCR (Constant Strain)	F_{50}	hr	>1000	>1000	>1000	>1000	>1000	>1000
Spiral Flow Length		mm	—	—	—	—	—	—

EXAMPLE 18 TO 22 AND COMPARATIVE EXAMPLE 7 TO 13

A one-step polymerization process shown in FIG. 3 was carried out with a 70 liter reaction vessel 1 equipped with a stirrer. The used solid catalyst was titanium tetrachloride which was supported on a solid carrier containing a component of anhydrous magnesium chloride. The one-step continuous polymerization was carried out under the conditions shown in Tables 9 to 11 to obtain higher molecular weight components A1 to A8 and lower molecular weight components B1 to B5. The total pressure of the polymerization in the reactor was 8.0 to 9.7 kg/cm^{2}G and the volume of liquid phase was 50 liter.

Polyethylene compositions were prepared by blending these polymerization products under the following conditions using a Banbury mixer. The properties of the obtained compositions were measured and the results of which are shown in the following Tables 13A to 14B as Examples and Comparative Examples.

BLENDING CONDITIONS

Under N_2 atmosphere, quantity of fed materials: 3 kg, revolution: 200 rpm, kneading time: 5 minutes, kneading temperature: 150° to 180° C.

In the next step, one-step polymerization was carried out under N_2 atmosphere using a 2 liter autoclave to obtain high molecular weight components A9 to A12. The polymerization conditions of this step are shown in Table 12. Polyethylene compositions were prepared from the thus obtained high molecular weight components A and the above low molecular weight components B using Brabender plastograph under the following conditions. The properties of the obtained compositions were measured, the results of which are shown in the following Tables 13A to 14B as Examples and Comparative Examples.

BLENDING CONDITIONS

Under N_2 atmosphere, quantity of fed materials: 70 kg, revolution: 20 rpm, kneading time: 7 minutes, kneading temperature: 160° C.

TABLE 9

One-Step Polymerization (1)						
			Higher Polymer Components A			
Items		Units	A1	A2	A3	A4
(Conditions)						
Qty. of Solvent		l/hr	25	25	25	25
Qty. of Ethylene		kg/hr	3.0	3.0	3.0	2.5
Qty. of Comonomer		l/hr	3.0	4.0	3.6	7.8
Kind of Comonomer		—	C_4	C_4	C_6	C_4
Qty. of Hydrogen		Nl/hr	14	7	13	10
Qty. of Solid Catalyst		g/hr	0.07	0.07	0.08	0.10
Qty. of Promoter (TEA)		mmol/hr	15	15	15	15
Ratio of Hydrogen/ethylene in Gas Phase Section		by mole	0.039	0.012	0.025	0.042
Ratio of Comonomer/Ethylene		by mole	0.13	0.17	0.15	0.36

TABLE 9-continued

Items		Units	One-Step Polymerization (1) Higher Polymer Components A A1	A2	A3	A4
in Gase Phase Section						
Polymerization Temperature		°C.	70	70	70	55
Polymerization Pressure		kg/cm²G	9.6	9.7	9.4	8.8
Polymerization Time		hr	1.6	1.6	1.6	1.6
(Physical Properties)						
Intrinsic Viscosity	η_1	dl/g	4.3	5.0	4.8	5.0
Melt Flow Rate	MFR	g/10 min	—	—	—	—
Density	d_1	g/cm³	0.919	0.914	0.918	0.900
Qty. Prepared	E_1	kg/hr	3.1	3.0	2.9	2.9
Ratio of Areas with TREF	S	—	0.8	1.2	0.9	3.7
Qty. soluble in 25° C. ODCB	W	wt. %	2.0	4.0	2.5	36.0

TABLE 10

Items		Units	One-Step Polymerization (2) Higher Polymer Components A A5	A6	A7	A8
(Conditions)						
Qty. of Solvent		l/hr	35	35	35	35
Qty. of Ethylene		kg/hr	4.2	4.1	4.1	4.2
Qty. of Comonomer		l/hr	0.49	0.61	0.58	—
Kind of Comonomer		—	C_4	C_4	C_6	—
Qty. of Hydrogen		Nl/hr	169	145	172	170
Qty. of Solid Catalyst		g/hr	0.30	0.45	0.45	0.30
Qty. of Promoter (TEA)		mmol/hr	21	11	11	21
Ratio of Hydrogen/ethylene in Gas Phase Section		by mole	0.69	0.81	0.85	0.70
Ratio of Comonomer/Ethylene in Gas Phase Section		by mole	0.032	0.045	0.030	—
Polymerization Temperature		°C.	80	80	80	80
Polymerization Pressure		kg/cm²G	9.4	8.0	8.6	9.6
Polymerization Time		hr	1.2	1.2	1.2	1.2
(Physical Properties)						
Intrinsic Viscosity	η_1	dl/g	1.22	1.05	1.00	1.31
Melt Flow Rate	MFR	g/10 min	7	17	23	5
Density	d_1	g/cm³	0.948	0.945	0.949	0.963
Qty. Prepared	E_1	kg/hr	4.1	3.8	4.0	4.0
Ratio of Areas with TREF	S	—	—	—	—	—
Qty. soluble in 25° C. ODCB	W	wt. %	—	—	—	—

TABLE 11

Items	Units	One-Step Polymerization (3) Lower Polymer Components B B1	B2	B3	B4	B4
(Conditions)						
Qty. of Solvent	l/hr	25	25	25	25	70
Qty. of Ethylene	kg/hr	2.8	2.9	2.7	2.0	4.0
Qty. of Comonomer	l/hr	2.6	2.6	1.9	8.5	0.1
Kind of Comonomer	—	C_4	C_6	C_4	C_4	C_4
Qty. of Hydrogen	Nl/hr	48	215	300	280	184
Qty. of Solid Catalyst	g/hr	0.2	0.3	0.3	0.5	1.8
Qty. of Promoter (TEA)	mmol/hr	15	15	15	15	21
Ratio of Hydrogen/ethylene in Gas Phase Section	by mole	0.71	1.74	3.09	2.01	1.96
Ratio of Comonomer/Ethylene in Gas Phase Section	by mole	0.23	0.17	0.18	0.45	0.003
Polymerization Temperature	°C.	70	70	70	60	80
Polymerization Pressure	kg/cm²G	8.8	11.0	12.7	14.5	12
Polymerization Time	hr	1.6	1.6	1.6	1.6	0.67
(Physical Properties)						
Intrinsic Viscosity	η_2	1.00	0.76	0.47	0.85	0.80
Density	d_2	0.918	0.925	0.920	0.910	0.960
Qty. Prepared	E_2	3.5	3.1	3.3	2.5	4.2

TABLE 12

Items	Units	One-Step Polymerization (4) Higher Polymer Components A A9	A10	A11	A12
(Conditions)					

TABLE 12-continued

Items		Units	One-Step Polymerization (4) Higher Polymer Components A A9	A10	A11	A12
Method of Polymerization Kind of Solvent			Solution Method Cyclo-hexane	Solution Method Cyclo-hexane	Solution Method Cyclo-hexane	Slurry Method Hexane
Qty. of Solvent		liter	1	1	1	1
Maintained Pressure of Ethylene		kg/cm^{2}G	20	20	20	7
Qty. of Comonomer		g	60	60	60	60
Kind of Comonomer		—	C_4	C_4	C_4	C_4
Qty. of Hydrogen		ml	150	150	150	150
Qty. of Solid Catalyst		mg	10	10	10	10
Qty. of Promoter (TEA)		mmol	0.5	0.5	0.5	0.5
Polymerization Temperature		°C.	170	170	170	170
Polymerization Pressure		kg/cm^{2}G	20	20	20	20
Polymerization Time		hr	1	1	1	1
(Physical Properties)						
Intrinsic Viscosity	η_1	dl/g	1.8	1.8	1.8	1.8
Density	d_1	g/cm^3	0.919	0.919	0.919	0.919
Qty. Prepared	E_1	g	91	87	83	96
Ratio of Areas with TREF	S	—	5.8	5.0	4.3	3.1
Qty. soluble in 25° C. ODCB	W	wt. %	2.2	3.6	2.4	11.9

TABLE 13A

Physical Properties of the Mixture of One-Step Polymerization Products (1A)

Items		Units	Examples 18	19	20	21	22
(Higher Molecular Weight Components A)							
Kind of Comonent A		—	A1	A2	A3	A4	A12
Intrinsic Viscosity	η_1	dl/g	4.3	5.0	4.8	5.0	1.8
Density	d_1	g/cm^3	0.919	0.914	0.918	0.900	0.919
Percentage	X_1	wt. %	50	45	50	33	50
Ratio of Areas with TREF	S	—	0.8	1.2	0.9	3.7	3.1
Qty. soluble in 25° C. ODCB	W	wt. %	2.0	4.0	2.5	36.0	11.9
S_1		—	1.80	2.07	1.69	4.00	4.4
W_1		wt. %	0.27	0.13	0.16	0.13	3.4
(Lower Molecular Weight Components B)							
Kind of Component B		—	B1	B2	B3	B4	B5
Intrinsic Viscosity	η_2	dl/g	1.00	0.76	0.47	0.85	0.80
Density	d_2	g/cm^3	0.918	0.925	0.920	0.910	0.960
Percentage	X_2	wt. %	50	55	50	67	50

TABLE 13B

Physical Properties of the Mixture of One-Step Polymerization Products (1B)

Items (Polyethylene Composition)		Units	Examples 18	19	20	21	22
Intrinsic Viscosity	η	dl/g	2.65	2.67	2.64	2.22	1.30
Melt Flow Rate	MFR	g/10 min	0.084	0.076	0.090	0.21	5
Density	d	g/cm^3	0.919	0.920	0.919	0.907	0.940
N-Value		—	2.23	2.41	2.43	2.39	1.75
Flow Parameter	FP	—	1.93	2.01	2.03	2.00	1.64
HLMFR/MFR		—	85	102	107	100	44
Yield Tensile Strength	YTS	kgf/cm^2	100	110	100	70	200
Tensile Impact Strength	TIS	kfg.cm/cm^2	940	1060	1280	980	70
Izod Impact Strength	IIS						
(23° C. 3mm)		kgf.cm/cm^2	NB	NB	NB	NB	6.0
(−40 C., 4 mm)		kgf.cm/cm^2	34	26	36	NB	4.2
Flexural Strength (Olsen)		kgf/cm^2	1900	2030	1960	1100	5000
Melt Tension	MT	g	14	15	14	9	—
Critical Shear Rate	γ_c	sec^{-1}	540	500	580	1200	—
Melting Point	T_m	°C.	120	121	120	120	126
ESCR (Constant Strain)	F_{50}	hr	>1000	>1000	>1000	>1000	—
Spiral Flow Length		mm	—	—	—	—	—

TABLE 14A

Physical Properties of the Mixture of One-Step Polymerization Products (2A)

Items		Units	Comparative Example 7	8	9	10	11	12	13
(Higher Molecular Weight Components A)									
Kind of Component A		—	A9	A10	A11	A5	A6	A7	A8
Intrinsic Viscosity	η_1	dl/g	1.8	1.8	1.8	1.22	1.05	1.00	1.31
Density	d_1	g/cm^3	0.919	0.919	0.919	0.948	0.945	0.949	0.963
Percentage	X_1	wt. %	50	50	50	100	100	100	100
Ratio of Areas with TREF	S	—	5.84	4.96	4.30	—	—	—	—
Qty. soluble in 25° C. ODCB	W	wt. %	2.2	3.6	2.4	—	—	—	—
S_1		—	4.4	4.4	4.4	—	—	—	—
W_1		wt. %	3.4	3.4	3.4	—	—	—	—
(Lower Molecular Weight Components B)									
Kind of Component B		—	B5	B5	B5	—	—	—	—
Intrinsic Viscosity	η	dl/g	0.80	0.80	0.80	—	—	—	—
Density	d_2	g/cm^3	0.960	0.960	0.960	—	—	—	—
Percentage	X_2	wt. %	50	50	50	0	0	0	0

TABLE 14B

Physical Properties of the Mixture of One-Step Polymerization Products (2B)

Items		Units	Examples 7	8	9	10	11	12	13
(Polyethylene Composition)									
Intrinsic Viscosity	η	dl/g	1.30	1.30	1.30	1.22	1.05	1.00	1.31
Melt Flow Rate	MFR	g/10 min	5	5	5	7	17	23	5
Density	d	g/cm^3	0.940	0.940	0.940	0.948	0.945	0.949	0.963
N-Value		—	1.72	1.74	1.73	1.56	1.47	1.47	1.56
Flow Parameter	FP	—	1.58	1.60	1.60	1.54	NG*	NG	1.55
HLMFR/MFR		—	38	40	40	34	NG	NG	35
Yield Tensile Strength	YTS	kgf/cm^2	200	200	200	260	240	270	310
Tensile Impact Strength	TIS	kgf · cm/cm^2	60	61	60	50	45	30	55
Izod Impact Strength	IIS								
(23° C., 3 mm)		kgf · cm/cm^2	5.0	5.0	5.0	5.0	4.0	3.0	4.2
(−40° C., 4 mm)		kgf · cm/cm^2	0.4	0.5	1.1	2.0	1.2	1.0	2.4
Flexural Strength (Olsen)		kgf/cm^2	4900	4900	5000	6600	7700	8000	11000
Melt Tension	MT	g	—	—	—	—	—	—	1.0
Critical Shear Rate	Y_c	sec^{-1}	—	—	—	—	—	—	4500
Melting Point	T_m	°C.	124	124	125	126	127	128	132
ESCR (Constant Strain)	F_{50}	hr	—	—	—	12	2	1	2.5
Spiral Flow Length		mm	—	—	—	420	560	600	420

NG*: Not good

Comparative Examples 14 to 20

Commercially available linear low molecular weight polyethylene of the following trademark were evaluated, the results of which are shown in the following Table 15 and 16.

(1) Phillips LLDPE #10: made by Phillips Petroleum Co.
(2) NUC G5221: made by Nippon Unicar
(3) Idemitsu PE-L 0234H: made by Idemitsu Petrochemical
(4) DSM LLDPE 1016: made by DSM
(5) CdF LOTREX FW1290: made by CdF

-continued

Comparative Examples 14 to 20

Commercially available linear low molecular weight polyethylene of the following trademark were evaluated, the results of which are shown in the following Table 15 and 16.

(6) Dow LLDPE XD60008-130: made by Dow Chemical Corp.
(7) Ultzex 2520L: made by Mitsui Petrochemcial Industry

TABLE 15

Physical Properties of Commercially Available LLDPE (1)

Items		Units	Comparative Example 14	15	16	17
Trademark		—	Phillips LLDPE #10	NUC G5221	Idemitsu PE-L 0234H	DSM LLDPE 1016
Polymerization Method		—	Slurry	Gas Phase	Solution	Solution
Intrinsic Viscosity	η	dl/g	1.75	1.53	1.54	1.70
Melt Flow Rate	MFR	g/10 min	0.95	1.97	1.96	1.19
Density	d	g/cm^3	0.921	0.920	0.920	0.918
N-Value		—	1.67	1.53	1.50	1.56
Flow Parameter	FP	—	1.57	1.46	1.44	1.49
HLMFR/MFR		—	37	29	28	31
Yield Tensile Strength	YTS	kgf/cm^2	110	105	105	105

TABLE 15-continued

Items		Units	Physical Properties of Commercially Available LLDPE (1) Comparative Example 14	15	16	17
Tensile Impact Strength	TIS	kgf · cm/cm²	460	320	320	900
Izod Impact Strength	IIS					
(23° C., 3 mm)		kgf · cm/cm²	NB	NB	NB	NB
(−40° C., 4 mm)		kgf · cm/cm²	2.5	2.3	2.5	2.8
Flexural Strength (Olsen)		kgf/cm²	2000	1900	1900	1700
Melt Tension	MT	g	2.0	1.0	1.0	2.0
Critical Shear Rate	Y_c	sec^{-1}	480	820	810	500
Melting Point	T_m	°C.	124	123	117	119
ESCR (Constant Strain)	F_{50}	hr	>1000	>1000	1000	>10000
Spiral Flow Length		mm	—	—	—	—

TABLE 16

Items		Units	Physical Properties of Commercially Available LLDPE (2) Comparative Example 18	19	20
Trademark		—	CdF LOTREX FW1290	Dow LLDPE XD60008-130	Mitsui Ultzex 2520L
Polymerization Method		—	High pressure ionic polym.	High Pressure ionic polym.	Solution polym.
Intrinsic Viscosity	η	dl/g	1.77	1.53	1.47
Melt Flow Rate	MFR	g/10 min	0.87	1.99	2.5
Density	d	g/cm³	0.919	0.919	0.921
N-Value		—	1.58	1.60	1.35
Flow Parameter	FP	—	1.50	1.52	1.33
HLMFR/MFR		—	32	33	21
Yield Tensile Strength	YTS	kgf/cm²	110	110	110
Tensile Impact Strength	TIS	kgf · cm/cm²	500	320	880
Izod Impact Strength	IIS				
(23° C., 3 mm)		kgf · cm/cm²	NB	NB	NB
(−40° C., 4 mm)		kgf · cm/cm²	3.3	3.3	1.5
Flexural Strength (Olsen)		kgf/cm²	1900	1900	2000
Melt Tension	MT	g	2.0	1.0	0.8
Critical Shear Rate	Y_c	sec^{-1}	380	950	700
Melting Point	T_m	°C.	119	116	122
ESCR (Constant Strain)	F_{50}	hr	>1000	>1000	>1000
Spiral Flow Length		mm	—	—	—

RESULTS OF EVALUATION

Low or medium density polyethylene compositions prepared by two-step polymerization method are described in Examples 1 to 10, 14 and 15 and Comparative Examples 1 to 3. Low density polyethylene compositions prepared by blending method are described in Examples 18 to 21. High density polyethylene compositions prepared by two-step polymerization method are described in Examples 11 to 13, 16 and 17 and Comparative Examples 4 to 6. High density polyethylene compositions prepared by blending method are described in Examples 22 and Comparative Examples 7 to 9. High density polyethylene compositions prepared by one-step polymerization method are described in Examples 10 to 13 and commercially available linear low density polyethylenes are described in Comparative Examples 14 to 20.

Among the above data, particularly important values are plotted in FIG. 4 to FIG. 8.

From these results, it will be understood that the polyethylene composition prepared according to the present invention is quite excellent in low temperature mechanical strength.

The polyethylene composition of the present invention has the properties of thermal stability, ESCR and elasticity comparable to the conventional polyethylene compositions, in addition, the composition of the present invention has the following advantages:

(1) The composition excels in low temperature mechanical properties such as low temperature Izod impact strength and other low temperature resistance.

(2) The composition excels in mechanical properties such as tensile strength, flexural strength, environmental stress cracking resistance and creep resistance.

(3) The workability such as high speed forming property is good because the composition excels in melt elasticity such as melt tension and low characteristics such as critical shear rate.

(4) With the above advantages, the polyethylene composition of the present invention can be used for producing various kinds of films, sheets, pipes, hollow containers, coating or wrapping materials and foamed articles. Furthermore, various kinds of molded goods can be produced because the polyethylene composition of the invention can be processed by any molding method such as extrusion molding, blow molding and injection molding.

What is claimed is:

1. A polyethylene composition which comprises:

(I) 20 to 80 wt. % of a copolymer of ethylene and α-olefins having 3 to 18 carbon atoms, which copolymer meets the following conditions (a) to (d):
(a) intrinsic viscosity (η_1) 1.2 to 9.0 dl/g
(b) density (d_1): 0.890 to 0.935 g/cm^3
(c) in the elution temperature-eluate volume curve in continuously temperature rising elution fractionation, the ratio S (Ib/Ia) of the area Ib under the curve of elution temperature of 25° to 90° C. to the area Ia under the curve of elution temperature of 90° C. and above, is not larger than the value S_1 which is calculated with the following equation,

$$S_1 = 20\,\eta_1^{-1}\exp[-50(d_1-0.900)]$$

(d) the quantity W wt. % of the content which is soluble in 25° C. o-dichlorobenzene is not smaller than the value W_1 which is calculated with the following equation,

$$W_1 = 20\exp(-\eta_1)$$

and

(II) 80 to 20 wt. % of ethylene homopolymer and/or the copolymer of ethylene and α-olefins having 3 to 18 carbon atoms, which meet the following conditions (e) and (f),
(e) intrinsic viscosity (η_2): 0.2 to 1.6 dl/g
(f) density (d_2): 0.890 to 0.980 g/cm^3 the value (η_1) is larger than (η_2), and the intrinsic viscosity (η) of the composition is 0.77 to 5.2 dl/g, the density (d) thereof is 0.890 to 0.950 g/cm^3 and the N-value calculated with the following equation is 1.7 to 3.5.

$$N\text{-Value} = \frac{\log(\dot{\gamma}_{150}/\dot{\gamma}_{20})}{\log(\tau_{150}/\tau_{20})}$$

wherein "$\dot{\gamma}$" is an apparent shear rate (sec^{-1} at 170° C.) and "τ" is an apparent shear stress (dyne/cm^2 at 170° C.) and the subscripts "20" and "150" indicates loads of 20 kg/cm^2 and 150 kg/cm^2.

2. The polyethylene composition as claimed in claim 1, wherein the α-olefin used for preparing said ethylene-α-olefin copolymer as said higher molecular weight component (I) is at least one member selected from the group consisting of 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene and 1-decene.

3. The polyethylene composition as claimed in claim 1, wherein said lower molecular weight component (II) is ethylene homopolymer.

4. The polyethylene composition as claimed in claim 1, wherein said lower molecular weight component (II) is a copolymer of ethylene and at least an α-olefin selected from the group consisting of 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene and 1-decene.

5. The polyethylene composition as claimed in claim 1 or 4, wherein said lower molecular weight component (II) is a mixture of ethylene homopolymer and ethylene-α-olefin copolymer.

* * * * *

US005206075A

United States Patent [19]

Hodgson, Jr.

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[45] Date of Patent: Apr. 27, 1993

[54] **SEALABLE POLYOLEFIN FILMS CONTAINING VERY LOW DENSITY ETHYLENE COPOLYMERS**

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[52] **U.S. Cl.** **428/216**; 428/349; 428/516; 428/500; 525/240

[58] **Field of Search** 428/516, 349, 500, 216; 525/240

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[57] **ABSTRACT**

The invention provides laminar polyolefin film materials having a base film layer comprising a blend of an olefin polymer and up to about 30% by weight of at least one very low density copolymer of ethylene and a C_3 to C_{20} alpha olefin comonomer copolymerizable with ethylene, said base layer having a heat sealable film layer present on one or both surfaces thereof comprising a very low density copolymer of ethylene and a copolymerizable C_5 to C_{12} alpha olefin comonomer. The ethylene copolymer constituents of the film are characterized as having a density in the range of about 0.88 g/cm^3 to abut 0.915 g/cm^3, a melt index in the range of about 0.5 dg/min to about 7.5 dg/min, a molecular weight distribution (M_w/M_n) of about 1.5 to about 3.5 and an essentially single melting point in the range of about 60° C. to about 115° C., measured as a DSC peak T_m.

Films of this invention exhibit extremely good hot tack seal strength at temperatures in the range of from about 200° to 290° F. thereby rendering them extremely useful as packaging materials in high speed packaging operations.

15 Claims, No Drawings

SEALABLE POLYOLEFIN FILMS CONTAINING VERY LOW DENSITY ETHYLENE COPOLYMERS

FIELD OF THE INVENTION

This invention relates to laminar polyolefin film materials having a base layer comprising a blend of an olefin polymer and a very low density ethylene/alpha monoolefin copolymer and at least one heat sealable layer present on one or both surfaces of said base layer, said heat sealable layer comprising a very low density copolymer of ethylene and a different alpha monoolefin.

DESCRIPTION OF RELATED ART

Films based on polyolefin polymers and copolymers are widely used in packaging applications which require sealing of the film to itself as the package is formed and/or filled. This sealing may be accomplished using adhesives such as low density polyethylene, ethylene/vinyl acetate copolymers and the like. When heat sealing is used, it is important that the thermoplastic film be readily heat sealable while also maintaining other physical and mechanical properties such as resistance to tearing, tensile strength and processability in high speed packaging equipment.

In form/fill packaging operations, film is generally first processed into a bag, a bottom being formed by squeezing together two films, and subjecting the bottom to a temperature above the seal initiation temperature under pressure to seal the bottom of the bag. The bag is subsequently filled with the goods to be packaged, and the top is then sealed in a similar fashion.

Film heat sealing is generally affected by means of heated flat surfaces, between which film surfaces are forcefully pressed together at a temperature above the seal initiation temperature of the film. When use is made of equipment such as vertical form, fill and seal machines, the bag is filled with the contents to be packaged while the bottom seal is still hot. Cooling the seal would entail too long a waiting time, thus lengthening the cycle time and increasing operating costs. Consequently, the film must be one which enables the formation of a strong seal even as the seal formed is at or near the seal formation temperature, i.e., it must have good hot tack seal strength.

There are several other desirable characteristics of a heat sealable film which enable trouble free performance in form fill and seal applications. First the film should provide strong seals at a low temperature to minimize energy requirements. Additionally, the film should allow for strong seals over a broad temperature range so that the film is more forgiving of heat sealing equipment adjustments and inadequacies. And further, the film should enable the development of seal strength almost immediately (before cooling) so that the seal bears and secures the weight of the wrapped product.

Many commonly used plastic materials which are used in the formation of film products could benefit from an improvement of their heat sealing characteristics. For example, crystalline polyolefin films such as polypropylene films have found extensive use in the field of packaging. Polypropylene films, in both oriented or non-oriented form, are used widely in packaging applications because of their superiority in mechanical properties such as tensile strength, rigidity, surface hardness, and optical properties such as gloss and transparency, and in food hygiene properties such as freedom from toxicity and odor. However, polypropylene and other crystalline polyolefin films typically require heat sealing initiation temperatures upwards of about 120° C. before adequate film seal strengths (at least 200 g/inch, desirably 400 g/inch and higher per specified settings for pressure and dwell time) are obtained. Consequently, there has been considerable development work to find ways that would allow the heat sealing of polypropylene films at lower temperatures and provide good hot tack seal strength. Such approaches have included the use of coatings, blend components and multiple film layers.

For example, EPA 0221726 discloses a film laminate prepared by coextruding a base layer which may be a polyolefin, particularly polypropylene or mixtures of polyolefins, and a heat seal layer which may be a very low density polyethylene (VLDPE) or a blend thereof with another polyolefin. The reference also indicates that scrap film may be recycled which could lead to structures where the base layer would comprise a blend of polypropylene and VLDPE.

The VLDPE is described as having a density of 0.890 to 0.912 g/cc and a melt index of generally 0.8 g/10 minutes or less, and is said to be of low crystallinity and produced in a low pressure process.

EPA 0247897 discloses a film laminate comprising a base layer which may contain polypropylene and at least one heat-sealable film layer which may be based on a very low density copolymer of ethylene and an alpha-monoolefin such as octene-1.

U.S. Pat. No. 4,764,404 discloses a multi layer package film having adhered to one side of a base layer (aluminum, polyamide or vinylidene chloride sheet) a composition comprising a blend of polypropylene (40–70% by weight), a second component which may be a copolymer of ethylene and a different alpha olefin (5–35% by weight) and a third elastomeric olefin polymer or copolymer (10–40% by weight).

The second component may be ethylene-based copolymers available from Mitsui under the designations "TAFMER" A or P.

EPA 0341 091 discloses that certain linear low density ethylene copolymers made in accordance with U.S. Pat. No. 4,612,300 using a Ziegler-Natta magnesium halide supported catalyst have good heat seal properties for packaging applications. These copolymers may contain 7–40 wt % of a C_5 to C_{12} alpha olefin and exhibit a density of 0.87 to 0.915.

In addition, U.S. Pat. No. 4,291,092 and divisionals, U.S. Pat. Nos. 4,339,496, 4,340,640 and 4,340,641, all disclose a heat sealable packaging film layer for a polypropylene substrate wherein the film layer comprises a blend of a copolymer of ethylene and a higher olefin and a copolymer of propylene and a higher olefin. U.S. Pat. No. 4,643,945 discloses the use of a linear low density polyethylene in a heat sealable film composition.

The prior art heat sealable films are not without certain deficiencies. A need still exists in the industry for a heat sealable layer having a seal initiation temperature of about 110° C. (225° F.) or lower while the film maintains good elevated temperature hot tack properties, abrasion resistance, blocking resistance, good strength and rigidity, and good film optical properties.

A class of highly active olefin catalysts known as metallocenes is well known especially in the preparation of polyethylene and ethylene copolymers. These catalysts, particularly those based on group IV B transi-

tion metals such as zirconium, titanium and hafnium, show extremely high activity in ethylene polymerization. The metallocene catalysts are also highly flexible in that, by manipulation of catalyst composition and reaction conditions, they can be made to provide polyolefins with controllable molecular weights from as low as about 200 (useful in applications such as lube oil additives) to about I million or higher as, for example, ultra high molecular weight linear polyethylene. At the same time, the molecular weight distribution of the polymers can be controlled from extremely narrow (as in a polydispersity, M_w/M_n of about 2), to broad (a polydispersity of about 8).

Exemplary of the development of these metallocene catalysts for the polymerization of ethylene is found in U.S. Pat. No. 4,937,299 to Ewen et al., hereby incorporated herein by reference. Among other things, this patent teaches that the structure of the metallocene catalyst includes an alumoxane which is formed when water reacts with trialkyl aluminum with the release of methane, which alumoxane complexes with the metallocene compound to form the catalyst.

There are a number of structural variables in polyolefins which affect the ultimate properties of the polymer. Two of the most important are composition distribution (CD) and molecular weight distribution (MWD). Composition distribution (CD) refers to the distribution of comonomer between copolymer molecules. This feature relates directly to polymer crystallizability, optical properties, toughness and many other important use characteristics. Molecular weight distribution (MWD) plays a significant role in melt processability as well as the level and balance of physical properties achievable. Molecular weight (MW) determines the level of melt viscosity and the ultimately desired physical properties of the polymer. The type and amount of comonomer effects the physical properties and crystallizability of the copolymer. All of these structural features (MW, MWD, CD, comonomer type and amount) are readily controllable through he use of metallocene catalysts as exemplified in U.S. Pat. No. 4,937,299, cited above.

Metallocene catalyst are particularly attractive in making tailored ultrauniform and super random specialty copolymers. For example, if a lower density ethylene copolymer is made with a metallocene catalyst, such as very low density polyethylene (VLDPE), an ultrauniform and super random copolymerization will occur, as contrasted with the polymer produced by copolymerization using a conventional Ziegler catalyst.

SUMMARY OF THE INVENTION

The invention provides laminar polyolefin film materials having a base film layer comprising a blend of an olefin polymer and up to about 30% by weight of at least one very low density copolymer of ethylene and a C_3 to C_{20} alpha monoolefin comonomer copolymerizable with ethylene, said base layer having a heat sealable film layer present on one or both surfaces thereof comprising a very low density copolymer of ethylene and a copolymerizable C_3 to C_{20} alpha olefin comonomer, said film further characterized in that the ethylene/alpha monoolefin copolymer present in one of said layers is a copolymer of ethylene and a C_6 C_{10} alpha monoolefin which alpha monoolefin differs from the alpha monoolefin present in the ethylene copolymer of the other said layers. The ethylene copolymer constituents of the film are characterized as having a density in the range of about 0.88 g/cm^3 to abut 0.915 g/cm^3, a melt index in the range of about 0.5 dg/min to about 7.5 dg/min, a molecular weight distribution (M_w/M_n) of about 1.5 to about 3.5 and an essentially single melting point in the range of about 60° C. to about 115° C., measured as a DSC peak T_m.

Films of this invention exhibit extremely good hot tack seal strength at temperatures in the range of from about 200° to 290° F. thereby rendering them extremely useful as packaging materials in high speed packaging operations.

DETAILED DESCRIPTION OF THE INVENTION

The polyolefin component of the base (or core) material of the film of this invention is preferably selected from the group consisting of polypropylene, low density polyethylene, linear low density polyethylene, polybutene, random copolymers of propylene with up to about 15 mole % of a C_2 or C_4 to C_{12} alpha olefin as well as blends of two or more of these materials. The polyolefins which may be used as the major component in the base layer are distinguished from the VLDPE copolymers also contained in the film in that the former generally exhibit a density in excess of about 0.915 g/cm^3.

The preferred polyolefin component of the base layer is crystalline polypropylene or random copolymers of propylene and another alpha olefin. Where random propylene copolymers are used as the base layer, the content of propylene is preferably in the range of from about 88 to 99 mole percent, based on total moles, more preferably in the range of about 90 mole percent to about 94 mole percent. The preferred random copolymers consist of propylene copolymerized with about 1 to 10 mole percent of ethylene.

The VLDPEs which may be used as the copolymer component of the base or sealing layers of the film of this invention are ethylene/alpha-monoolefin copolymers wherein the monoolefin can have from 3–20 carbon atoms such as ethylene/butene-1, ethylene/hexene-1, ethylene/octene-1, ethylene/propylene copolymers. These ethylene copolymers with prescribed range of comonomer levels can be prepared by polymerization of the suitable olefins in the presence of supported or unsupported metallocene catalysts systems. The preferred range of comonomer level generally ranges from about 4 to about 15 mole percent.

The low melting polymer ingredient utilized in the base layer and heat seal layer of the film of the present invention has a density in the range of about 0.88 g/cm^3 to about 0.915 g/cm^3. Preferably the density is in the range of about 0.89 g/cm^3 to about 0.91 g/cm^3. Densities above about 0.90 g/cm^3 are measured using standard accepted procedures. At densities below about 0.90 g/cm^3, the samples are additionally conditioned by holding them for 48 hours at ambient temperature (23° C.), prior to density measurement.

The melt index (MI) of the ethylene/alpha-monoolefin copolymers of the present invention is in the range of about 0.5 dg/min to about 7.5 dg/min. Preferably the MI is in the range of about 0.5 dg/min to about 5.0 dg/min, and the most preferred MI is in the range of 1.0 to 2.5 dg/min. MI as measured herein is determined according to ASTM D-1238 (190/2.16). High load MI is determined according to ASTM D-1238 190/21.6). These copolymers also have a narrow molecular weight distribution. The ratio of M_w/M_n is generally in the

range of about 1.5 to about 3.5, preferably in the range of about 2.0 to about 3.0.

The ethylene/alpha-monoolefin copolymers should also have an essentially single melting point characteristic with a peak melting point (T_m) as determined by Differential Scanning Colorimetry (DSC) in the range of about 60° C. to about 115° C. Preferably the DSC peak T_m is in the range of about 80° C. to about 100° C. "Essentially single melting point" as used herein means that at least about 80% by weight of the material corresponds to a single T_m peak existing in the range of about 60°–115° C., and there is essentially absent from the polymer any substantial fraction of material which corresponds to a T_m peak found at a temperature higher than about 115° C. i.e., "essentially" the bulk material content of the polymer corresponds to a "single" melting point peak in the 60°–115° C. range, and "essentially" no substantial fraction of the material has a peak melting point in excess of about 115° C., as determine by DSC analysis.

DSC measurements are made on a perkin Elmer System 7 Thermal Analysis System. Melting information reported are second melting data i.e. the sample in heated at a programmed rate of 10° C./min to a temperature above its melting range. The sample is then cooled at a programmed rate of 10° C./min to a temperature below its crystallization range. The sample is then reheated (2nd melting) at a programmed rate of 10° C./min.

The presence of higher melting peaks is detrimental to film properties such as haze, and compromises the chances for meaningful reduction in the seal initiation temperature of the final film.

The composition distribution breadth index (CDBI) of such VLDPE copolymers will generally be in the range of about 70 percent or higher. The CDBI is defined as the weight percent of the copolymer molecules having a comonomer content within 50 percent (i.e. ±50%) of the median total molar comonomer content. The CDBI of linear polyethylene, which does not contain a comonomer, is defined to be 100%.

The Composition Distribution Breadth Index (CDBI) is determined via the technique of Temperature Rising Elution Fractionation (TREF). CDBI determination clearly distinguishes the VLDPE copolymers of this invention (narrow composition distribution as assessed by CDBI values generally above 70%) from VLDPEs available commercially today which generally have a broad composition distribution as assessed by CDBI values generally less than 55%. The benefits to the subject invention accrue through the specific use of VLDPEs of narrow composition distribution. The CDBI of a copolymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation as described, for example, Wild et al., *J. Poly. Sci, Poly, Phys. Ed., Vol.*, 20, p. 441 (1982). Unless otherwise indicated, terms such as "comonomer content", "average comonomer content" and the like refer to the bulk comonomer content of the indicated copolymer.

Utilizing a metallocene catalyst, the VLDPE copolymers useful as the low melting polymers of the present invention can be produced in accordance with any suitable polymerization process, including a slurry polymerization, gas phase polymerization, and high pressure polymerization process.

A slurry polymerization process generally uses superatomospehric pressures and temperatures in the range of 40°–100° C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The liquid employed in the polymerization medium can be an alkane, cycloalkane, or an aromatic hydrocarbon such as toluene, ethylbenzene or xylene. The medium employed should be liquid under the conditions of polymerization and relatively inert. Preferably, hexane or toluene is employed.

Alternatively, the VLDPE copolymer components of the present invention may be formed by gas-phase polymerization. A gas-phase process utilizes superatmospheric pressure and temperatures in the range of about 50°–120° C. Gas phase polymerization can be performed in a stirred or fluidized bed of catalyst and product particles in a pressure vessel adapted to permit the separation of product particles from unreacted gases. Ethylene, comonomer, hydrogen and an inert diluent gas such as nitrogen can be introduced or recirculated so as to maintain the particles at a temperatures of 50° C.–120° C. Triethylaluminum may be added as needed as a scavenger of water, oxygen, and other impurities. Polymer product can be withdrawn continuously or semicontinuously at a rate such as to maintain a constant product inventory in the reactor. After polymerization and deactivation of the catalyst, the product polymer can be recovered by any suitable means. In commercial practice, the polymer product can be recovered directly from the gas phase reactor, freed of residual monomer with a nitrogen purge, and used without further deactivation or catalyst removal.

The VLDPE copolymers of the present invention can also be produced in accordance with a high pressure process by polymerization ethylene in combination with other monomers such as butene-1, hexene-1, octene-1, or 4-methylpentene-1 in the presence of the catalyst system comprising a cyclopentadienyl-transistion metal compound and an alumoxane compound. It is important, in the high-pressure process, that the polymerization temperature be above about 120° C. but below the decomposition temperature of the polymer product and that the polymerization pressure be above about 500 bar (kg/cm^2). In those situations wherein the molecular weight of the polymer product that would be produced at a given set of operating conditions is higher than desired, any of the techniques known in the art for control of molecular weight, such as the use of hydrogen or reactor temperature, may be used in the process of this invention.

The blend composition of the film base layer contains from about 1 to about 30 percent by weight of the VLDPE copolymer component, more preferably from about 5 to abut 25 percent by weight of VLDPE, each based on the total weight of olefin polymer forming the base film layer.

The VLDPE copolymer which is applied to one or both surfaces of the base film layer to form a heat sealable layer possesses the same physical and chemical characteristics and may be made by the same processes as described above with respect to the VLDPE component of the base layer, except that it differs compositionally from the copolymers contained in the base layer.

It has been found that the excellent results in terms of hot tack seal strength are achieved where the VLDPE component of a first layer which may be the base layer or heat sealable layer is a copolymer of ethylene and a C_3 to C_{20} alpha-monoolefin and the VLDPE compo-

nent of the other layer is a copolymer of ethylene and a C_6 to C_{10} alpha-monoolefin which differs from the alpha-monoolefin comonomer present in the VLDPE of the first layer. In the more preferred embodiments of the invention, the C_6 to C_{10} alpha-monoolefin-containing copolymer is used as the heat seal layer and the different C_3 to C_{20} alpha-monoolefin-containing copolymer is used as a component in the base layer.

These materials provide an excellent balance of adhesion to the substrate base film without the need to employ an interdisposed anchor or tie layer such as polyvinylidene chloride or ethylene/vinyl acetate copolymers, and also possess the requisite high hot tack seal strength required for modern high speed packaging applications. Best results in terms of adhesion and hot tack seal strength are achieved with laminar structures wherein the VLDPE copolymer component of the base layer is an ethylene/butene-1 copolymer and the heat seal coating layer comprises a copolymer of ethylene with either hexene-1 or octene-1.

The percent hexane extractables for the low melting polymer VLDPE ingredients of the present invention are low enough to allow for applications in the food industry. Preferably, for food packaging applications, products having extractables 5 percent and under would be utilized.

The heat sealable films of the present invention may be manufactured using film fabrication technologies well known in the art. For example, the base film may be extruded into film using a flat die or blown extruded into film using a tubular die, and the heat seal layer formed thereon by solvent deposition, lamination or coextrusion techniques. A preferred method of manufacture is via coextrusion wherein a molten layer of the heat seal material is applied to the surface of an extruded cast film of the base layer. These laminar films may optionally be further oriented (either uniaxially or biaxially) using technologies well known to those skilled in the art.

The laminar film structure of the present invention may have an overall thickness in the range of from about 0.5 mil to about 5 mil, with a preferred thickness of about 0.75 mil to about 2.5 mil. The heat seal coating layer may constitute from about 3 to about 50% of this overall thickness, more preferably from about 10 to 25% of the overall thickness, present on one or both sides of the base layer.

The VLDPE copolymer component of the base layer may also comprise a mixture of compositionally different VLDPE components within the scope of this invention. This is particularly the case because the VLDPE component of the base layer differs compositionally from the VLDPE component of the heat seal layer. Scrap trim recycled to the extruder and mixed with virgin polymer used to make the base layer will result in a base layer which contains a mixture of these VLDPE copolymers. Thus, in a preferred embodiment wherein the heat sealable layer comprises a VLDPE copolymer of ethylene and hexene-1 and the base layer contains a VLDPE copolymer of ethylene and butene-1, recycle of scrap trim back to the extruder would result in a base layer containing a mixture of the ethylene/butene-1 and ethylene/hexene-1 copolymers, along with the major polyolefin component of the base layer.

The polymer components used to fabricate the films of the present invention may also contain appropriate amounts of other additives normally included in such compositions. These include slip agents such as talc, antioxidants, fillers, dyes, pigments, radiation stabilizers and like additives.

The film products made in accordance with the present invention are useful in a wide variety of bag and pouch applications in which heat sealability is important. Bag and pouch forming include, but are not limited to horizontal form-fill-and-seal, and vertical form-fill-and-seal.

Some key properties of the final film are heat sealability and seal strength, hot tack strength, tensile strength, film rigidity, haze and gloss, low extractables, and abrasion resistance.

EXAMPLES

Example I

Preparation of VLDPE-EB-1 (1.6 MI, Density of 0.8895, butene-1 Comonomer)

A catalyst is prepared by adding 5.1 liters of a 10% solution of trimethylaluminum in heptane into a dry and oxygen-free two-gallon reactor equipped with a mechanical stirrer. 800 g of undehydrated silica gel, containing 12.3% water, is slowly added into the reactor. After the addition is complete, the mixture is stirred at ambient temperature for one hour. 20 g of di-(n-butylcyclopentadienyl) zirconium dichloride slurried in 30 liters of heptane is then added into the reactor and the mixture is allowed to react at ambient temperature for 30 minutes. The reactor is then heated to 65° C., while a nitrogen gas is purged through the reactor to remove the solvent. The nitrogen purging is stopped when the mixture in the reactor turns into a free-flowing powder.

The polymerization was conducted in a 16-inch diameter fluidized gas phase reactor. Ethylene, butene-1 and nitrogen were fed continuously into the reactor to maintain a constant production rate. Product was periodically removed from the reactor to maintain the desired bed weight. The polymerization conditions are shown below.

Gas Phase Polymerization	
Temperature (°F.)	137
Total Pressure (psia)	300
Gas Velocity (ft/sec)	1.58
Catalyst Feed Rate (g/hr)	7.0
Butene-1 Feed Rate (lb./hr)	5.3
Production Rate (lb/hr)	26

The polymerized product had a Melt Index (dg/min.) of 1.60 and a Density (g/cm^3) of 0.8895.

Example 2

Preparation of VLDPE-EB-2 (2.3 MI, Density of 0.8970, butene-1 comonomer)

The process of Example 1 was repeated as set forth therein except that the polymerization conditions were as shown below:

Gase Phase Polymerization	
Temperature (°F.)	129
Total Pressure (psia)	300
Gas Velocity (ft/sec)	1.59
Catalyst Fed Rate (g/hr)	7.0
Butene-1 Feed Rate (lb./hr)	2.9
Production Rate (lb./hr)	19

The polymerized product had a Melt Index (dg/min.) of 2.30 and a Density (g/cm^3) of 0.8970.

Example 3

Preparation of VLDPE-EH (15 MI, Density of 0.905, hexene-1 comonomer)

The catalyst for polymerizing this ethylene copolymer was prepared as follows. An 800 gram quantity of silica gel and a 2700 ml. aliquot of methylalumoxane/-toluene solution (10%) were placed in a two-gallon reactor and allowed to react at ambient temperature for one hour. A 21.6 gram quantity of di-(n-butylcyclopentadienyl) zirconium dichloride slurried in 300 ml of toluene was added into the reactor and the mixture was allowed to react at 65° C. for 30 minutes. The reactor was then heated at 75° C. while nitrogen gas was purged through the reactor to remove the solvent. The heating and nitrogen purging were stopped when the mixture in the reactor turned into a free-flowing powder.

The polymerization was conducted in a 16-inch diameter fluidized bed gas-phase reactor. ethylene, hexene-1 and nitrogen were fed continuously into the reactor to maintain a constant production rate. Product was periodically removed from the reactor to maintain the desired bed weight. The polymerization conditions are shown below:

Gas Phase Polymerization	
Temperature (°F.)	158
Total Pressure (psia)	300
Gas Velocity (ft/sec)	1.22
Catalyst Feed Rate (g/hr)	3.0
Hexene-1 Feed Rate (lb./hr)	3.1
Production Rate (lb./hr)	20

The polymerized product had a measured Melt Index (dg/min) of 1.5 and a density of 0.905 g/cm^3.

Examples 4–12

A series of coextruded unoriented films were produced on a compounding extruder to produce AB type laminar films comprising a base film layer having an average thickness of 1.6 mil and a single heat sealable coating layer having an average thickness of 0.4 mils, i.e., the coating layer constituted about 20% of the thickness of the composite film. The composition of the base films was either polypropylene, a propylene/ethylene random copolymer or a mixture of one of the above with a VLPDE copolymer of ethylene and butene-1 as prepared in Examples 1 and 2. The composition of the coating layer was either a VLDPE copolymer of ethylene and butene-1 or a VLDPE copolymer of ethylene and hexene-1 as prepared in accordance with Example 3. The composition of these various layers is identified in Table 1.

As used in Table "PEC" is a crystallizable random copolymer of propylene having a MFI of 5.0 dg/min and containing abut 5 wt % ethylene. It has a DSC peak melting temperature of about 132° C. and is available commercially from Exxon Chemical Company as Excorene TM PD-9282. PP is a crystallizable polypropylene homopolymer having an MFI of about 2.3 dg/min and is available from Exxon Chemical Company under the designation Exorcene TM PP4092. The material identified as EB-1 is a VLDPE copolymer of ethylene and butene-1 as prepared in Example 1 having a MFI of 1.60 dg/min and a density of 0.8895 g/cm^3. The material designated as EB-2 is a VLDPE prepared in Example 2 with a MFI of 2.30 dg/min and a density of 0.8970 g/cm^3. The material designated EH is a VLDPE copolymer of ethylene and hexene-1 as prepared in Example 3 having an MFI of 1.5 dg/min and a density of 0.905 g/cm^3.

The material designated EVA is a copolymer of ethylene and vinyl acetate (28% by weight vinyl acetate content) having an MFI of 3.1 dg/min.

Heat seal data and hot tack seal strengths of the various film formulations and configurations were evaluated using a Thellar Model EB Heat Sealer. Under this test, the heat seal sides of the coated films are brought into contact and seals are attempted to be formed at various temperatures from 140° F. to 300° F. in 10°F. increments. The dwell time and pressures applied during sealing generally ranges from about 0.25 to 0.5 seconds and 65–80 psi respectively. The times and pressures employed are indicated in Table 1.

Test results are shown in Table 1. As is evident from the data in Table 1, film compositions within the scope of this invention (Examples 8 and 9) exhibited hot tack strengths in excess of 625 g/in over a sealing temperature of 240° to 270° F. and over 700 g/in at sealing temperatures of 240° F. This is in marked contrast to other formulations outside the scope of the present invention wherein the sealing layer and base layer each contain a VLDPE copolymer of ethylene and butene-1 or a copolymer of ethylene and vinyl acetate.

TABLE 1

EXAMPLE	BASE FILM COMPOSITION	VLDPE COATING COMPOSITION	DWELL TIME (SEC)	SEAL PRESSURE (PSI)	SEAL STRENGTH (g/IN) AT °F. 200°	210°	220°	230°	240°	250°	260°	270°
4	100% PEC —	EB-1	0.5	67	<25	<25	25	<25	<25	<25	<25	<25
5	80% PEC 20% EB-1	EB-1	0.5	70	25	25	<25	<25	<25	<25	<25	<25
6	80% PP 20% EB-1	EB-1	0.5	70	NS*	NS	<25	25	<25	<25	<25	<25
7	100% PEC —	EB-2	0.5	70	NS	<25	<25	<25	<25	<25	<25	<25
8	100% PP —	EB-2	0.5	67	NS	<25	25	25	75	25	25	25
9	80% PP 20% EB-1	EH	0.25	70	NS	100	425	>700	>700	>700	>700	>700
10	80% PP 20% EB-1	EH	0.5	76	25	225	375	550	>700	625	675	675
11	100% PEC —	EVA	0.5	70	(MAX SEAL STRENGTH AT 160° F.; <25 ABOVE 200° F.)							
12	100% PEC —	EVA	0.25	70	(MAX SEAL STRENGTH AT 170° F.; <75 ABOVE 200° F.)							

*NS MEANS NO SEAL

I claim:

1. A multiple layer heat sealable film comprising a base layer and a heat sealable layer superimposed on one or both sides of said base layer;

said base layer comprising a blend of (a) an olefin polymer having a density in excess of 0.915 g/cm^3 and (b) from about 1 to about 30 weight percent based on base layer polymer content of a copolymer of ethylene and a C_3 to C_{20} alpha monoolefin comonomer, said copolymer having a density of from about 0.88 to about 0.915 g/cm^3, a melt index of from about 0.5 to about 7.5 dg/min, a molecular weight distribution of no greater than about 3.5 and a composition distribution breadth index greater than about 70 percent;

said heat sealable layer comprising a copolymer of ethylene and a C_3 to C_{20} alpha-monoolefin comonomer, said copolymer having a density of from about 0.88 to about 0.915 g/cm^3, a melt index of from about 0.5 to about 7.5 dg/min, a molecular weight distribution of no greater than about 3.5 and a compositional breath index greater than about 70 percent, said film further characterized in that the ethylene/alpha-monoolefin copolymer present in one of said layers is a copolymer of ethylene and a C_6 to C_{10} alpha-monoolefin which alpha-monoolefin differs from the alpha-monoolefin comonomer present in the copolymer of the other said layers.

2. The film of claim wherein said copolymer of ethylene and C_6 to C_{10} alpha-monoolefin is present in said heat sealable layer.

3. The film of claim 2 wherein said film has a thickness in the range of from about 0.5 to about 5.0 mils.

4. The film of claim 2 wherein said heat sealable layer constitutes about 3 to about 50% of the thickness of said film.

5. The film of claim 2 wherein said ethylene copolymer present in each layer contains from about 4 to about 15 mole percent of said comonomer.

6. The film of claim 2 wherein said heat sealable layer comprises a copolymer of ethylene and hexene-1.

7. The film of claim 6 wherein said base layer comprises a copolymer of ethylene and butene-1.

8. The film of claim 2 wherein the olefin polymer component of said base layer is selected from the group consisting of polypropylene, random copolymers of propylene with up to about 15 mole % of a C_2 or C_4–C_{12} alpha olefin, low density polyethylene, linear low density polyethylene, high density polyethylene, polybutene and mixtures thereof.

9. The film of claim 8 wherein the olefin polymer component of said base layer is polypropylene.

10. The film of claim 8 wherein the olefin polymer component of said base layer is a crystallizable random copolymer of propylene and ethylene.

11. The film of claim 2 wherein each of said ethylene copolymers present in said base layer and said heat sealable layer are prepared using a metallocene catalyst system.

12. The film of claim 2 wherein said heat sealable layer is superimposed on only one side of said base layer.

13. The film of claim 12 wherein said heat sealable layer comprises about 20% of the thickness of the composite film.

14. A process for fabricating a heat sealed package comprising contacting the surfaces of the heat sealable layers of a film in accordance with claim 1 with one another and under conditions of temperature and pressure sufficient to bond said heat sealable layers together.

15. The process of claim 14 wherein said temperature ranges from about 210° to about 270° F.

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US005218071A

United States Patent [19]

Tsutsui et al.

[11] Patent Number: 5,218,071

[45] Date of Patent: Jun. 8, 1993

[54] ETHYLENE RANDOM COPOLYMERS

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[58] Field of Search 526/160, 348, 348.2, 526/348.3, 348.5, 348.6

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[57] ABSTRACT

In accordance with the present invention, there are provided ethylene copolymers composed of structural units (a) derived from ethylene and structural units (b) derived from α-olefin of 3~20 carbon atoms, said ethylene copolymers having

[A] a density of 0.85~0.92 g/cm^3,

[B] an intrinsic viscosity [η] as measured in decalin at 135° C. of 0.1~10 dl/g,

[C] a ratio ($\overline{M}w/\overline{M}n$) of a weight average molecular weight ($\overline{M}w$) to a number average molecular weight ($\overline{M}n$) as measured by GPC of 1.2~4, and

[D] a ratio (MFR_{10}/MFR_2) of MFR_{10} under a load of 10 kg to MFR_2 under a load of 2.16 kg at 190° C. of 8~50, and being narrow in molecular weight distribution and excellent in flowability.

7 Claims, 4 Drawing Sheets

FIG. 1

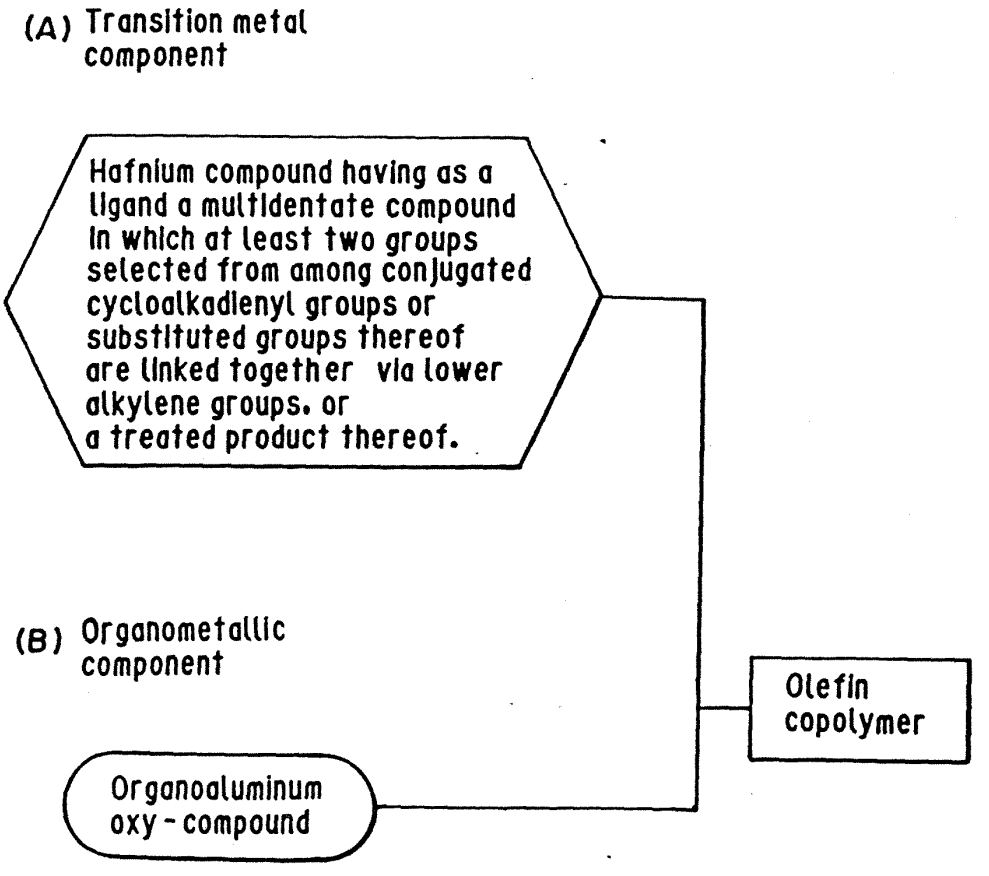

(A) Transition metal component
Hafnium compound having as a ligand a multidentate compound in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups, or a treated product thereof.
(B) Organometallic component
Organoaluminum oxy-compound
Olefin copolymer

FIG.2

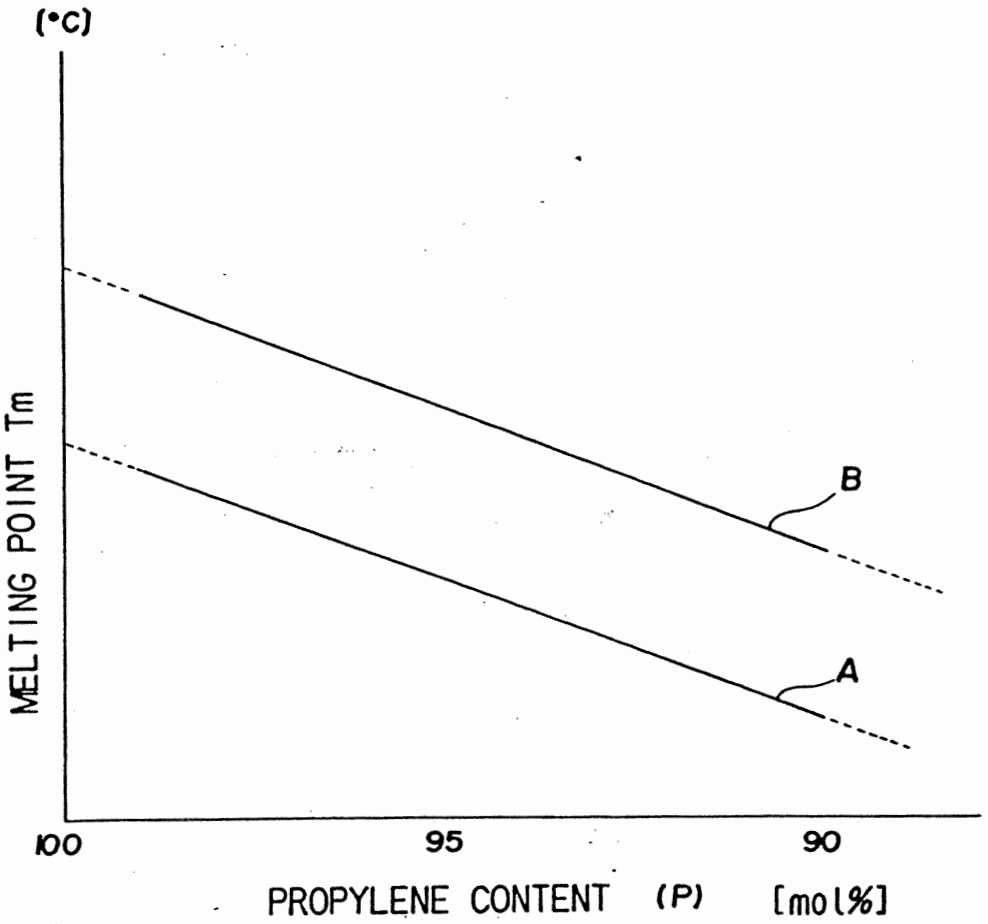


FIG.3

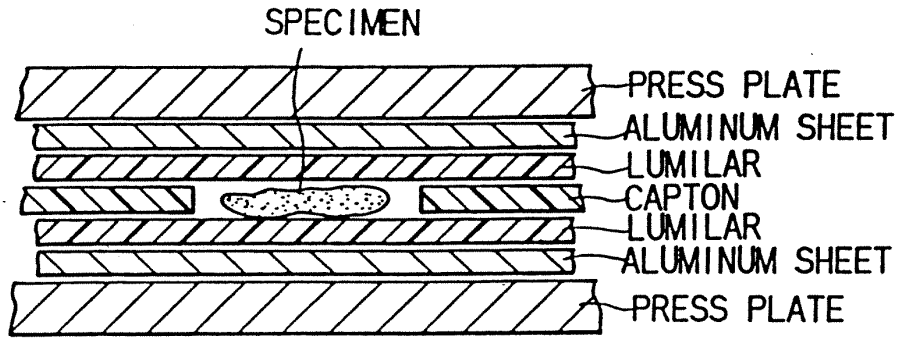

SPECIMEN
PRESS PLATE
ALUMINUM SHEET
LUMILAR
CAPTON
LUMILAR
ALUMINUM SHEET
PRESS PLATE

FIG.4

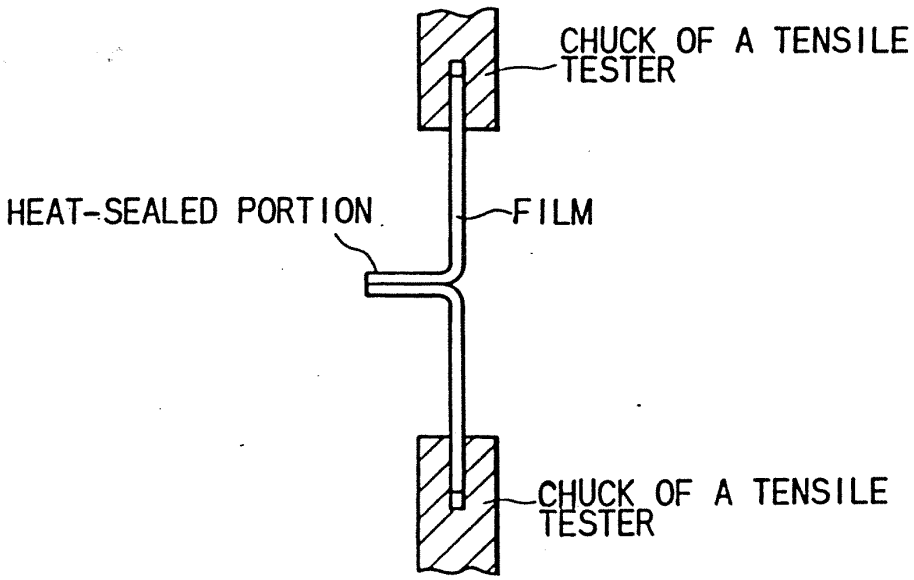
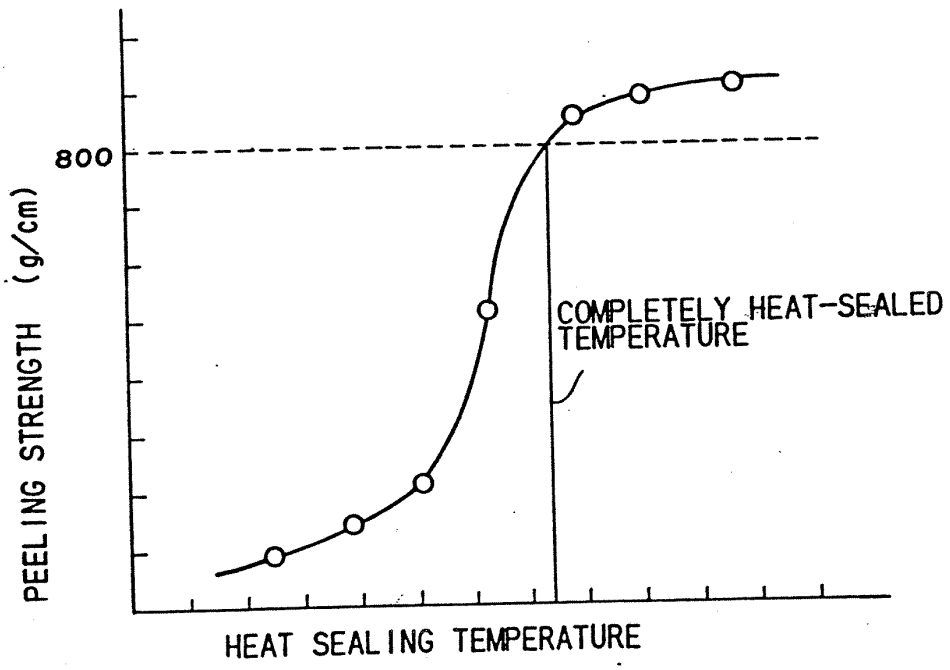

CHUCK OF A TENSILE TESTER
HEAT-SEALED PORTION
FILM
CHUCK OF A TENSILE TESTER

FIG.5


800
PEELING STRENGTH (g/cm)
COMPLETELY HEAT-SEALED TEMPERATURE
HEAT SEALING TEMPERATURE

ETHYLENE RANDOM COPOLYMERS

This application is a continuation of application Ser. No. 07/459,834, filed Jan. 31, 1990, now abandoned.

FIELD OF THE INVENTION

This invention relates to novel ethylene copolymers and a process for preparing the same and more particularly to novel ethylene copolymers excellent in flowability in spite of the fact that they are narrow in molecular weight distribution ($\overline{M}w/\overline{M}m$) in comparison with conventionally known ethylene copolymers, and to a process for preparing the same.

In a further aspect, the invention relates to novel propylene random copolymers and a process for preparing the same and more particularly to novel propylene random copolymers having low melting points in comparison with conventionally known propylene random copolymers and, in particular, excellent in heat-sealing properties and anti-block properties, and to a process for preparing the same.

In another aspect, the invention, relates to olefin polymerization catalysts capable of polymerizing olefins with excellent polymerization activity even when the amount of aluminoxane used is reduced and capable of giving olefin polymers having high molecular weights.

BACKGROUND OF THE INVENTION

When molded into articles such as film, copolymers of ethylene and α-olefins of 3 to 20 carbon atoms are found to have excellent mechanical strength such as tensile strength, tear strength or impact strength and also excellent heat resistance, stress crack resistance, optical characteristics and heat-sealing properties in comparison with conventional high-pressure low density polyethylenes, and are known as materials particularly useful for the preparation of inflation film or the like.

Generally speaking, the ethylene copolymers mentioned above have such excellent characteristics that when said copolymers come to be narrower in molecular weight distribution represented by the ratio ($\overline{M}w/\overline{M}n$) of weight average molecular weight ($\overline{M}w$) to number average molecular weight ($\overline{M}n$), the molded articles obtained therefrom, such as film, are found to be less tacky. However, when these ethylene copolymers having a narrow molecular weight distribution are melted, there were such drawbacks that their flowability represented by the ratio (MFR_{10}/MFR_2) of MFR_{10} under a load of 10 kg to MFR_2 under a load of 2.16 kg as measured at 190° C. is small, with the result that they become poor in moldability.

Therefore, if ethylene copolymers which are small in value of $\overline{M}w/\overline{M}n$ and narrow in molecular weight distribution and, moreover, large in value of MFR_{10}/MFR_2 and excellent in flowability come to be obtained, such ethylene copolymers are certainly of great commercial value.

On the other hand, polypropylene has wide applications in the field of plastics because of its excellent physical properties. For example, polypropylene is widely used as packaging film material. In the applications of the type, however, because of its relatively high melting point, polypropylene is generally copolymerized with ethylene or α-olefins of 4 to 20 carbon atoms in order to improve heat-sealing properties at low temperature, and is used in the form of propylene/α-olefin copolymer.

Packaging films formed from these known propylene/α-olefin copolymers are still not sufficient in heat-sealing properties, though they are excellent in transparency and scratch resistance in comparison with those formed from low density polyethylene, and accordingly it is hoped that propylene/α-olefin copolymers excellent in heat-sealing properties even at lower temperatures will come to be obtained.

It is well known that the above-mentioned propylene/α-olefin random copolymers may be improved in heat-sealing properties by increasing the proportion of ethylene or α-olefin of 4 to 20 carbon atoms to propylene in the copolymer, However, if the proportion of ethylene or α-olefin of 4 to 20 carbon atoms is increased in the copolymerization, the resulting propylene/α-olefin copolymer increases in amount of the solvent-soluble component, whereby the resultant copolymers come to be poor in anti-blocking properties and also in stiffness.

Such propylene/α-olefin random copolymers excellent in heat-sealing properties, anti-block properties and stiffness as mentioned above are available only when they have a low melting point in spite of the fact that the proportion of α-olefin in the copolymer is small.

Incidentally, olefin polymerization catalysts composed generally of titanium compounds or vanadium compounds and organoaluminum compounds have heretofore been used for preparing ethylene copolymers. In recent years, however, catalysts composed of zirconium compounds and aluminoxane have been proposed of late as new Ziegler polymerization catalysts. Japanese Patent L-O-P Publn. No. 19309/1983 discloses a process for polymerizing ethylene and one or two more C_3–C_{12} α-olefins at a temperature of from −50° C. to 200° C. in the presence of a catalyst composed of a transition metal containing compound represented by the following formula

$$(\text{Cyclopentadienyl})_2\text{MeRHal}$$

wherein R is cyclopentadienyl, C_1–C_6 alkyl or halogen, Me is a transition metal, and Hal is halogen, and a linear aluminoxane represented by the following formula

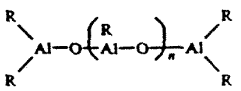
$$Al_2OR_4(Al(R)—O)_n$$

wherein R is methyl or ethyl, and n is a number of 4–20, or a cyclic aluminoxane represented by the following formula

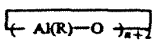
$$\left[\leftarrow Al(R)—O\rightarrow\right]_{n+2}$$

wherein R and n are as defined above. The publication cited above describes that ethylene should be polymerized in the presence of small amounts, up to 10% by weight, of somewhat long chain α-olefins or mixtures thereof in order to control a density of the resulting polyethylene.

Japanese Patent L-O-P Publn. No. 95292/1984 discloses an invention relating to a process for preparing a linear aluminoxane represented by the following formula

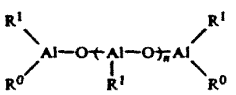


wherein n is 2–40, and R is C_1–C_6 alkyl, and cyclic aluminoxane represented by the following formula,



wherein n and R are as defined above. The publication cited above describes that olefins are polymerized in the presence of the aluminoxane prepared by the process of said publication, for example, methyl aluminoxane in admixture with a bis(cyclopentadienyl) compound of titanium or zirconium, whereupon at least twenty-five million g of polyethylene per 1 g of the transition metal per hour is obtained.

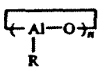
Japanese Patent L-O-P Publn. No. 35005/1985 discloses a process for preparing olefin polymerization catalysts, wherein an aluminoxane compound represented by the following formula



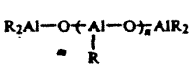
wherein R^1 is C_1–C_{10} alkyl, and R^0 is R^1 or represents -O- by linkage therewith, is first allowed to react with a magnesium compound, the resulting reaction product is then chlorinated, followed by treating with a Ti, V, Zr or Cr compound. This publication cited above describes that the catalysts prepared by the process of said publication are particularly useful for the copolymerization of mixtures of ethylene and C_3–C_2 α-olefins.

Japanese Patent L-O-P Publn. No. 35006/1985 discloses a combination of (a) mono-, di- or tri-cyclopentadienyl of two or more different transition metals or derivatives thereof and (b) aluminoxane as a catalyst system for preparing reactor blend polymers. Example 1 of the above-cited publication discloses that polyethylene having a number average molecular weight of 15,300, a weight average molecular weight of 36,400 and containing 3.4% of the propylene component has been obtained by polymerization of ethylene with propylene in the presence of a combination of bis(pentamethylcyclopentadienyl)zirconium dimethyl and aluminoxane as the catalyst. Example 2 of the said publication discloses polymerization of ethylene with propylene in the presence of a combination of bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(methylcyclopentadienyl)zirconium dichloride and aluminoxane as the catalyst, whereby a blend of polyethylene and ethylene/propylene copolymer is obtained, said polyethylene having a number average molecular weight of 2,000, a weight average molecular weight of 8,300 and the propylene content of 7.1 mol%, and comprising a toluene-soluble portion having a number average molecular weight of 2,200, a weight average molecular weight of 11,900 and the propylene content of 30 mol% and a toluene-insoluble portion having a number average molecular weight of 3,000, a weight average molecular weight of 7,400 and the propylene content of 4.8 mol%. Similarly, Example 3 of the said publication discloses a blend of LLDP and an ethylene/propylene copolymer, said LLDPE comprising a soluble portion having a molecular weight distribution ($\overline{M}w/\overline{M}n$) of 4.57 and the propylene content of 20.6% and an insoluble portion having the molecular weight distribution of 3.04 and the propylene content of 2.9 mol%.

Japanese Patent L-O-P Publn. No. 35007/1985 discloses a process for polymerizing ethylene alone or together with α-olefins of at least 3 carbon atoms in the presence of a catalyst system containing metallocene and a cyclic aluminoxane represented by the following formula



wherein R is alkyl of 1–5 carbon atoms, and n is an integer of 1 to about 20, or a linear aluminoxane represented by the following formula



wherein R and n are as defined above. According to the said publication, the polymers obtained by the above-mentioned process are alleged to have a weight average molecular weight of from about 500 to about 1,400,000 and a molecular weight distribution of 1.5–4.0.

Japanese Patent L-O-P Publn. No. 35008/1985 discloses polyethylene or copolymers of ethylene and C_3–C_{10} α-olefins, both having a broad molecular weight distribution, obtained by using a catalyst system containing at least two kinds of metallocenes and aluminoxane. The said copolymers disclosed in the above-mentioned publication are alleged to have a molecular weight distribution ($\overline{M}w/\overline{M}n$) of 2–50.

Japanese Patent L-O-P Publn. No. 130314/1986 discloses polypropylene high in isotacticity obtained by polymerization of propylene in the presence of a catalyst system comprising a sterically fixed zirconium-chelate compound and aluminoxane.

J. Am. Chem. Soc., 109, 6544 (1987) discloses formation of a high molecular weight isotactic polypropylene obtained by polymerization of propylene in the presence of a catalyst system comprising ethylenebis(indenyl)hafnium dichloride or its hydride and aluminoxane, said isotactic polypropylene having a narrow molecular weight ($\overline{M}w/\overline{M}n$) of 2.1–2.4.

Japanese Patent L-O-P Publn. No. 142005/1987 discloses a stereoblock polypropylene having $\overline{M}w/\overline{M}n$ of 5.0–14.9 obtained by polymerization of propylene in the presence of a catalyst system comprising tetramethylethylenebis(cyclopentadienyl) titanium chloride and aluminoxane. The polypropylene thus obtained is short in isotactic chain length and is a rubbery polymer.

The present inventors have come to accomplish the present invention on the basis of their finding that ethylene copolymers which are small in $\overline{M}w/\overline{M}n$ and narrow in molecular weight distribution and, moreover, large in MFR_{10}/MFR_2 and excellent in flowability are obtained by copolymerization of ethylene with α-olefins of 3–20 carbon atoms in the presence of olefin polymerization catalysts composed of specific hafnium compounds and organoaluminum oxy-compounds.

Furthermore, the present inventors have found that when propylene and α-olefins of 4–20 carbon atoms are copolymerized in the presence of olefin polymerization catalysts composed of specific hafnium compounds and aluminoxane, there are obtained propylene/α-olefin copolymers which are narrow in molecular weight distribution and small in amount of the α-olefin copolymerized therewith, but are low in melting point in comparison with conventionally known propylene/α-olefin copolymers, on which the present invention has been based.

Accordingly, the present invention is to solve such problems associated with the prior art as mentioned above, and an object of the invention is to provide ethylene copolymers which are small in $\overline{M}w/\overline{M}n$ and narrow in molecular weight distribution and, moreover, which are large in MFR_{10}/MFR_2 and excellent in flowability, and processes for preparing the same.

A further object of the invention is to provide propylene/α-olefin copolymers which are narrow in molecular weight distribution and small in amount of the α-olefin copolymerized therewith but have a low melting point and, moreover, which are excellent in heat-sealing properties and also excellent in anti-block properties and stiffness, and processes for preparing the same.

Another object of the invention is to provide olefin polymerization catalysts, which produce polymers which are narrow in molecular weight distribution in homopolymerization or narrow in molecular weight and composition distribution in copolymerization with high polymerization activities even by the use of small amounts of aluminoxane, furthermore, produce easily polymers which are high in molecular weight.

DISCLOSURE OF THE INVENTION

The ethylene copolymers of the present invention are those having (a) structural units derived from ethylene and (b) structural units derived from α-olefin of 3–20 carbon atoms, which are characterized in that they have

(i) a density of 0.85–0.92 g/cm^3,

(ii) an intrinsic viscosity [β] of 0.1–10 dl/g as measured in Decalin (decahydronaphthalene) at 135° C.,

(iii) a ($\overline{M}w/\overline{M}n$) ratio of a weight average molecular weight ($\overline{M}w$) to a number average molecular weight ($\overline{M}n$) of 1.2–4 as measured by GPC, and

(iv) a (MFR_{10}/MFR_2) ratio of MFR_{10} under a load of 10 kg to MFR_2 under a load of 2.16 kg of 8–50 as measured at 190° C.

The processes for preparing ethylene copolymers of the present invention are characterized in that ethylene and α-olefins of 3–20 carbon atoms are copolymerized so that a density of the resulting copolymers becomes 0.85–0.92 g/cm^3, in the presence of catalysts formed from

[A] hafnium compounds having multidentate coordination compounds as ligands, in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups, or hafnium compounds obtained by treating the above-mentioned hafnium compounds with alkylsilylated silica gel, and

[B] organoaluminum oxy-compounds.

The first propylene/α-olefin random copolymers of the present invention are those having (a) structural units derived from propylene and (b) structural units derived from α-olefins of 4–20 carbon atoms, which are characterized in that they have

(i) 90–99 mol% of said structural units (a) and 1–10 mol% of said structural units (b),

(ii) an intrinsic viscosity [η] of 0.5–6 dl/g as measured in Decalin (dehydronaphthalene) at 135° C.,

(iii) a melting point [Tm], as measured by a differential scanning calorimeter, falling within the range of the formula $90<Tm<155-3.5$ (100-P) wherein P is the propylene component (mol%) contained in the copolymer,

(iv) a ($\overline{M}w/\overline{M}n$) ratio of less than 3.5 between a weight average molecular weight ($\overline{M}w$) and a number average molecular weight ($\overline{M}n$) as measured by GPC, and

(v) a boiling trichloroethylene-insoluble matter in an amount of less than 5% by weight.

The processes for preparing the first propylene/α-olefin copolymers of the present invention are characterized in that propylene and α-olefins of 4–20 carbon atoms are copolymerized at a temperature of 40°–100° C. so that the resulting copolymers have 90–99 mol% of structural units (a) derived from propylene and 1–10 mol% of structural units (b) derived from the α-olefin, in the presence of catalysts formed from

[A] hafnium compounds having multidentate coordination compounds as ligands, in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups, and

[B] organoaluminum oxy-compounds.

The second propylene/α-olefin random copolymers of the present invention are those having (a) structural units derived from propylene, (b) structural units derived from ethylene and (c) structural units derived from α-olefins of 4–20 carbon atoms, which are characterized in that they have

(i) 90–99 mol% of said structural units (a), 0.5–9.5 mol% of said structural units (b) and 0.5–9.5 mol% of said structural units (c),

(ii) an intrinsic viscosity [η] of 0.5–6 dl/g as measured in decalin at 135° C.,

(iii) a melting point [Tm], as measured by a differential scanning calorimeter, falling within the range of the formula $70<Tm<155-5.5$ (100-P) wherein P is the propylene component (mol%) contained in the copolymer, and

(iv) a boiling trichloroethylene-insoluble matter in an amount of less than 5% by weight.

The processes for preparing the second propylene/α-olefin copolymers of the present invention are characterized in that propylene, ethylene and α-olefins of 4–20 carbon atoms are copolymerized so that the resulting copolymers have 90–99 mol% of structural units (a) derived from propylene, 0.5–9.5 mol% of structural units (b) and 0.5–9.5 mol% of structural units (c), in the presence of catalysts formed from

[A] hafnium compounds having multidentate coordination compounds as ligands in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups, and

[B] organoaluminum oxy-compounds.

In accordance with the present invention, there are provided olefin polymerization catalysts formed from

[A] hafnium compounds having multidentate coordination compounds as ligands in which at least two groups selected from conjugated cycloalkadienyl

groups or substituted groups thereof are linked together via lower alkylene groups,

[B] organoaluminum oxy-compounds, and

[C] organoaluminum compounds.

In accordance with the present invention, furthermore, there are provided olefin polymerization catalysts formed from

[A] hafnium compounds having multidentate coordination compounds as ligands in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups,

[B-1] organoaluminum oxy-compounds formed from tri-n-alkyl aluminum, and

[B-2] organoaluminum oxy-compounds in which at least one hydrocarbon group other than n-alkyl group is bonded to Al atom.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an illustration of the process for the preparation of the olefin copolymers of the present invention.

FIG. 2 is a graph showing the relationship between the propylene content and melting point of the propylene random copolymer of the present invention.

FIGS. 3-5 are stepwise illustrative of the method of evaluation of heat-sealing properties of the propylene random copolymer of the present invention.

BEST MODE OF PRACTICING THE INVENTION

The ethylene copolymers of the present invention and processes for preparing the same are illustrated below in detail.

The process for the preparation of the ethylene copolymers of the present invention is illustratively shown in FIG. 1

The ethylene copolymers of the invention are random copolymers of ethylene and α-olefins of 3-20 carbon atoms. The ethylene copolymers have a density of 0.85-0.92 g/cm^3, preferably 0.85-0.91 g/cm^3 and especially 0.85 0.90 g/cm^3.

In this connection, the density of these ethylene copolymers was measured by gradient tube density determination using the strand of ethylene copolymer used at the time of determining MFR_2 under a load of 2.16 kg at 190° C.

In these ethylene copolymers, are present desirably structural units (a) derived from ethylene in an amount of 60-96 mol%, preferably 65-95 mol% and especially 70-94 mol%, and structural units (b) derived from α-olefin of 3-20 carbon atoms in an amount of 4-40 mol%, preferably 5-35 mol% and especially 6-30 mol%.

The composition of the copolymer is determined by measuring a spectrum of ^{13}C-NMR of a specimen obtained by dissolving about 200 mg of the copolymer in 1 ml of hexachlorobutadiene in a test tube of 10 mmϕ under the conditions of a measurement temperature of 120° C., measurement frequency of 25.05 MHz, spectrum width of 1500 Hz, pulse repetition time of 4.2 sec. and pulse width of 6 sec.

Alpha olefins of 3-20 carbon atoms used in the present invention include propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, etc.

The ethylene copolymers of the present invention desirably have an intrinsic viscosity [η] of 0.1-10 dl/g, preferably 0.5-6 dl/g as measured in decalin at 135° C.

The molecular weight distribution ($\overline{M}w/\overline{M}n$) as obtained by gel permeation chromatography (GPC) of the ethylene copolymers of the invention is 1.2-4, preferably 1.4-3.5 and especially 1.5-3.0. As is evidenced by the foregoing, the ethylene copolymers of the invention are narrow in molecular weight distribution and excellent in anti-block properties.

In this connection, a value of ($\overline{M}w/\overline{M}n$) obtained in the invention was determined by the following procedure in accordance with Takeuchi, "Gel Permeation Chromatography," Maruzen, Tokyo.

(1) Using a standard polystyrene having the known molecular weight (a monodispersed polystyrene produced and sold by Toyo Soda K.K.), molecular weight M and GPC (Gel Permeation Chromatography) count of the sample are measured to prepare a correlation diagram calibration curve of the molecular weight M and EV (Elution Volume). The concentration of the sample used is maintained at 0.02% by weight.

(2) GPC chromatograph of the sample is taken by GPC measurement, and a number average molecular weight $\overline{M}n$ and a weight average molecular weight $\overline{M}w$, in terms of polystyrene, are calculated from the calibration curve mentioned in the above procedure (1) to obtain a value of $\overline{M}w/\overline{M}n$. In that case, the conditions under which the sample is prepared, and the conditions under which GPC measurement is conducted are as follows:

Preparation of sample

(a) The sample is put in an Erlenmeyer flask together with o-dichlorobenzene so that the same amounts to 0.1% by weight.

(b) The Erlenmeyer flask is heated at 140° C. and stirred for about 30 minutes to dissolve the sample in o-dichlorobenzene.

(c) The solution is subjected to GPC.

GPC measurement conditions

The measurement was conducted under the following conditions.

(a) Apparatus	150C-ALC/GPC manufactured by Waters Co.
(b) Column	GMH Type manufactured by Toyo Soda K.K.
(c) Amount of sample	400 μl
(d) Temperature	140° C.
(e) Flow rate	1 ml/min

In the ethylene copolymers of the invention, a (MFR_{10}/MFR_2) ratio of MFR_{10} at 190° C. under a load of 10 kg to MFR_2 at 190° C. under a load of 2.16 kg is 8-50, preferably 8.5-45 and especially 9-40.

Such ethylene copolymers having the MFR_{10}/MFR_2 ratio falling within the range of 8-50 as mentioned above are quite favorable in flowability at the time when they are melted.

In contrast thereto, the aforementioned known ethylene copolymers having the $\overline{M}w/\overline{M}n$ ratio of 1.2-4 will come to have the MFR_{10}/MFR_2 ratio in the range of 4-7, and hence they are poor in flowability at the time when they are melted.

As mentioned above, the ethylene copolymers of the present invention have such excellent characteristics that they have a small molecular weight distribution ($\overline{M}w/\overline{M}n$), and molded articles resulting therefrom are

less sticky and, at the same time, they are large in MFR_{10}/MFR_2 and excellent in flowability at the time when they are melted.

The ethylene copolymers of the invention as illustrated above may be prepared by copolymerization of ethylene with α-olefins of 3–20 carbon atoms so that the resulting copolymers have a density of 0.85–0.92 g/cm^3 in the presence of catalysts formed from

[A] hafnium compounds having multidentate coordination compounds as ligands in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene, or hafnium catalyst components obtained by treating the above-mentioned hafnium compounds with alkylsilylated silica gel, and

[B] organoaluminum oxy-compounds.

The catalyst components [A] used in the invention are hafnium compounds having multidentate coordination compounds as ligands in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof, e.g. indenyl group, substituted indenyl group and partially hydrated compounds thereof, are linked together via lower alkylene groups, or compounds obtained by treating the above-mentioned hafnium compounds with alkylsilylated silica gel.

The above-mentioned hafnium compounds include, for example, the following compounds.

Ethylenebis(indenyl)dimethyl hafnium,
Ethylenebis(indenyl)diethyl hafnium,
Ethylenebis(indenyl)diphenyl hafnium,
Ethylenebis(indenyl)methyl hafnium monochloride,
Ethylenebis(indenyl)ethyl hafnium monochloride,
Ethylenebis(indenyl)methyl hafnium monobromide,
Ethylenebis(indenyl)hafnium dichloride,
Ethylenebis(indenyl)hafnium dibromide,
Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dimethyl hafnium,
Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)methyl hafnium monochloride,
Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)hafnium dichloride,
Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)hafnium dibromide,
Ethylenebis(4-methyl-1-indenyl)hafnium dichloride,
Ethylenebis(5-methyl-1-indenyl)hafnium dichloride,
Ethylenebis(6-methyl-1-indenyl)hafnium dichloride,
Ethylenebis(7-methyl-1-indenyl)hafnium dichloride,
Ethylenebis(5-methoxy-1-indenyl)hafnium dichloride,
Ethylenebis(2,3-dimethyl-1-indenyl)hafnium dichloride,
Ethylenebis(4,7-dimethyl-1-indenyl)hafnium dichloride,
Ethylenebis(4,7-dimethoxy-1-indenyl)hafnium dichloride.

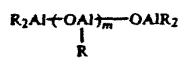
The above-mentioned hafnium compounds may contain small amounts of zirconium or titanium. In such a case, the content of zirconium or titanium is less than 1% by weight, preferably less than 0.7% by weight and especially less than 0.5% by weight.

The hafnium catalyst components used in the present invention may include compounds obtained by treating the above-mentioned hafnium compounds with alkylsilylated silica gel. More particularly, the said hafnium catalyst components may be hafnium compound solutions which are obtained, for example, by passing a solution of the above-mentioned hafnium compound in an organic solvent such as toluene through a column packed with alkylsilylated silica gel, wherein said hafnium compound is brought into contact with the alkylsilylated silica gel.

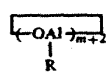
The organic solvents used in that case are preferably aromatic hydrocarbons such as toluene, benzene and xylene. The alkylsilylated silica gel used may include those obtained by treating silica gel with dimethyl dichlorosilane, ethylmethyl dichlorosilane, trimethyl chlorosilane, trimethyl bromosilane, divinyl dichlorosilane, diethyl dichlorosilane or methylpropyl dichlorosilane. The hafnium concentration in the hafnium compound solution is usually from 1×10^{-5} to 5×10^{-3} mol/l, and the amount of the alkylsilated silica gel used is usually 20–500 g per 1 mmol of the hafnium compound. A temperature at which the hafnium compound solution is brought into contact with the alkylsilylated silica gel is usually 0°–50° C.

When the hafnium catalyst components obtained by treating the above-mentioned hafnium compounds with the alkylsilylated silica gel are used as the catalyst components [A], ethylene copolymers excellent in transparency are obtained.

The catalyst components [B] used in the process of the present invention are organoaluminum oxy-compounds. The organoaluminum oxy-compounds used as the catalyst components may be shown as benzene-soluble aluminoxanes represented by the following general formulas (1) and (II).



(I)



(II)

wherein R may be the same or different and is a hydrocarbon group such as methyl, ethyl, propyl or butyl, preferably methyl or ethyl and especially methyl, and m is an integer of at least 2, preferably at least 5. The above-mentioned aluminoxanes may be prepared, for example, by the procedures as exemplified below.

(1) A procedure which comprises reacting a suspension in a hydrocarbon medium of a compound containing water of absorption or a salt containing water of crystallization, for example, magnesium chloride hydrate, copper sulfate hydrate, aluminumsulfate hydrate, nickel sulfate hydrate or serous chloride hydrate, with trialkylaluminum.

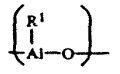
(2) A procedure which comprises reacting trialkylaluminum directly with water, water vapor or ice in a medium such as benzene, toluene, ethyl ether and tetrahydrofuran.

The aluminoxanes as illustrated above may contain small amounts of organometallic components.

Further, the organoaluminum oxy-compounds used in the present invention may be those which are insoluble in benzene. The benzene-insoluble organoaluminum oxy-compounds are illustrated hereinafter.

The benzene-insoluble organoaluminum oxy-compounds used in the invention may be prepared by (i) reaction of organoaluminum compounds with water or (ii) reaction of solutions of aluminoxane, for example, hydrocarbon solutions thereof, with water or active hydrogen-containing compounds.

The benzene-insoluble organoaluminum oxy-compounds are considered to have alkyloxyaluminum units represented by the formula



wherein R^1 is hydrocarbon of 1~12 carbon atoms and Al component soluble in benzene at 60° C. is in an amount, in terms of Al atom, of less than 10%, preferably less than 5% and especially less than 2%, thus they are insoluble or sparingly soluble in benzene.

Solubility in benzene of the organoaluminum oxy-compounds of the present invention is determined by suspending the organoaluminum oxy-compound equivalent to Al of 100 mg atom in 100 ml of benzene, stirring the suspension at 60° C. for 6 hours, filtering the thus treated suspension at a temperature elevated to 60° C. using G-5 glass filter equipped with a jacket, washing 4 times the solids portion separated on the filter with 50 ml of benzene kept at 60° C. and then measuring the amount of Al atoms (× mmol) present in the total filtrate.

In the alkyloxyaluminum units mentioned above, R^1 is methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, pentyl, hexyl, octyl, decyl, cyclohexyl, cyclooctyl, etc. Among these, preferred are methyl and ethyl, particularly methyl.

In addition to the alkyloxyaluminum units of the formula



the benzene-insoluble organoaluminum oxy-compounds of the invention may contain oxyaluminum units represented by the formula



In the above-mentioned formulas, R^1 is as defined previously, R^2 is hydrocarbon of 1~12 carbon atoms, alkoxyl of 1~12 carbon atoms aryloxy of 6~20 carbon atoms, hydroxyl, halogen or hydrogen, and R^1 and R^2 represent the groups different from each other. In that case, the benzene-insoluble organoaluminum oxy-compounds are preferably those containing the alkyloxyaluminum units



in the proportion of at least 30 mol%, preferably at least 50 mol% and especially at least 70 mol%.

The organoaluminum compounds (i) used for preparing such benzene-insoluble organoaluminum oxy-compounds as mentioned above are those represented by the formula $R^1_nAlX_{3-n}$ wherein R^1 is hydrocarbon of 1~12 carbon atoms, X is halogen, alkoxyl of 1~12 carbon atoms, aryloxy of 6~20 carbon atoms or hydrogen, and n is 2~3.

Such organoaluminum compounds (i) as mentioned above include trialkylaluminum such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisopropylaluminum, tri-n-butylaluminum, tri-sec-butylaluminum, tri-tertbutylaluminum, tripentylaluminum, trihexylaluminum, trioctylaluminum, tridecylaluminum, tricyclohexylaluminum and tricycloctylaluminum; dialkylaluminum halides such as dimethylaluminum chloride, dimethylaluminum bromide, diethylaluminum chloride, diethylaluminum bromide, and diisobutylaluminum chloride; dialkylaluminum hydrides such as diethylaluminum hydride and diisobutylaluminum hydride; dialkylaluminum alkoxides such as dimethylaluminum methoxide and diethylaluminum ethoxide; and dialkylaluminum aryloxides such as diethylaluminum phenoxide. Of these organoaluminum compounds, preferred are those of the above-mentioned general formula in which R^1 is alkyl and X is chlorine, and particularly preferred is trialkylaluminum.

In this connection, isoprenylaluminum of the general formula $(i\text{-}C_4H_9)_xAl_y(C_5H_{10})_z$ wherein x, y and z are each positive integer, and $z \geqq 2x$ may also used as the organoaluminum compound (i).

The organoaluminum compounds (i) as illustrated above may be used either singly or in combination.

The active hydrogen-containing compounds (ii) used in preparing the benzene-insoluble organoaluminum oxy-compounds of the present invention include alcohols such as methyl alcohol and ethyl alcohol, and diols such as ethylene glycol and hydroquinone.

When water is used in preparing the benzene-insoluble organoaluminum oxy-compounds of the present invention, the water may be used after dissolving or suspending in hydrocarbon solvents such as benzene, toluene and hexane, ether solvents such as tetrahydrofuran, and amine solvents such as triethylamine, or may be used in the form of water vapor or ice. As the water, moreover, there may also be used water of crystallization of salt such as magnesium chloride, magnesium sulfate, aluminum sulfate, copper sulfate, nickel sulfate, iron sulfate and cerrous chloride, or water of adsorption adsorbed to inorganic compounds such as silica, alumina and aluminum hydroxide or polymers.

As mentioned above, the benzene-insoluble organoaluminum oxy-compounds of the present invention may be prepared by reaction of the organoaluminum compound (i) with water, or by reaction of a solution of aluminoxane, for example, a hydrocarbon solution thereof, with water or the active hydrogen containing compound. In preparing the benzene-insoluble organoaluminum oxy-compound from the organoaluminum compound and water, the organoaluminum compound is brought into contact with water in a solvent, for example, a hydrocarbon solvent, and in that case, the water is added to the reaction system so that the organoaluminum atoms dissolved in the reaction system become less than 20% based on the total organoaluminum atom. In obtaining the benzene-insoluble organoaluminum oxy-compounds according to the procedure as mentioned above, it is desirable that the water is brought into contact with the organoaluminum compound in the proportion of 1~5 moles, preferably 1.5~3 moles of the water to 1 mole of the organoaluminum compound.

The above-mentioned reaction for forming the benzene-insoluble organoaluminum oxy-compounds is car-

ried out in solvents, for example, hydrocarbon solvents. The solvents used include aromatic hydrocarbons such as benzene, toluene, xylene, cumene and cymene, aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, octane, decane, dodecane, hexadecane and octadecane, alicyclic hydrocarbons such as cyclopentane, cyclooctane, cyclodecane and cyclododecane, such hydrocarbon solvents, for example, petroleum fractions, as gasoline, kerosine and gas oil, halides of the above-mentioned aromatic hydrocarbons, aliphatic hydrocarbons and alicyclic hydrocarbons, especially chlorides and bromides thereof, and ethers such as ethyl ether and tetrahydrofuran. Among these hydrocarbon media as exemplified above, particularly preferred are aromatic hydrocarbons.

A concentration in terms of Al atom of the organoaluminum compound in the reaction system is desirably 1×10^{-3} to 5 gram atom/l preferably 1×10^{-2} to 3 gram atom/l, and a concentration in the reaction system of water such as water of crystallization is usually 1×10^{-3} to 20 mol/l, preferably 1×10^{-2} to 10 mol/l. In that case, it is desirable that the organoaluminum atoms dissolved in the reaction system are less than 20%, preferably less than 10% and especially in the range of from 0 to 5% based on the total organoaluminum atom.

Contact of the organoaluminum compound with water may be carried out, for example, by the following procedures.

(1) A procedure wherein a hydrocarbon solution of organoaluminum is brought into contact with a hydrocarbon solvent containing water.

(2) A procedure wherein water vapor is blown into a hydrocarbon solution of organoaluminum, thereby bringing the organoaluminum into contact with the water vapor.

(3) A procedure wherein a hydrocarbon solution of organoaluminum is mixed with a hydrocarbon suspension of a compound containing water of adsorption or a compound containing water of crystallization, thereby bringing the organoaluminum into contact with the water of adsorption or water of crystallization.

(4) A procedure wherein a hydrocarbon solution of organoaluminum is brought into contact with ice.

The above-mentioned reaction of the organoaluminum with water is carried out usually at a temperature of from −100° to 150° C., preferably −50° to 100° C. and especially −30° to 80° C. The reaction time, though it may largely vary depending upon the reaction temperature, is usually from 1 to 200 hours, preferably 2 to 100 hours.

In preparing the benzene-insoluble organoaluminum oxy-compounds from a solution of aluminoxane and water or a active hydrogen-containing compound, the aluminoxane present in the solution of aluminoxane is brought into contact with water or the active hydrogen-containing compound.

The solution of aluminoxane is a solution of aluminoxane in such a solvent as used in forming the above-mentioned benzene-insoluble organoaluminum oxy-compounds, preferably aromatic hydrocarbons such as benzene and toluene, and this solution may contain other components so long as they do not affect adversely the reaction between the aluminoxane and water or the active hydrogen-containing compound.

The amount of water or the active hydrogen-containing compound used in the above-mentioned reaction is 0.1 to 5 moles, preferably 0.2 to 3 moles based on 1 gram atom of aluminum present in the solution of aluminoxane. A concentration in the reaction system of aluminoxane in terms of aluminum atom is usually 1×10^{-3} to 5 gram atom/l, the reaction system of water is usually 2×10^{-4} to 5 mole/l, preferably 2×10^{-3} to 3 mole/l.

Taking, as an example, the reaction of the solution of aluminoxane with water, said solution of aluminoxane is brought into contact with water or the active hydrogen-containing compound, for example, by the following methods.

(1) A method which comprises bringing the solution of aluminoxane into contact with a hydrocarbon solvent containing water.

(2) A method which comprises blowing water vapor into the solution of aluminoxane, thereby bringing the aluminoxane present in the solution of aluminoxane into contact with the water vapor.

(3) A method which comprises mixing the solution of aluminoxane with a hydrocarbon solution of a compound containing water of adsorption or a compound containing water of crystallization, thereby bringing the aluminoxane present in the solution of aluminoxane into contact with the water of adsorption or water of crystallization.

(4) A method which comprises bringing the solution of aluminoxane into contact directly with water or ice.

The above-mentioned procedures may also be applied to the case wherein the active hydrogen-containing compound (ii) is used instead of water.

The reaction of the solution of aluminoxane with water or the active hydrogen-containing compound as illustrated above may be carried out usually at a temperature of from −50° to 150° C., preferably 0° to 120° C. and especially 20°~100° C. The reaction temperature, though it may largely vary depending upon the reaction temperature, is usually 0.5~300 hours, preferably about 1~150 hours.

In preparing the ethylene copolymers by using the olefin polymerization catalysts as mentioned above, a concentration in the polymerization system of the hafnium compound in terms of hafnium atom is usually 10^{-8} to 10^{-2} gram atom/l, preferably 10^{-7} to 10^{-3} gram atom/l.

The above-mentioned organoaluminum oxy-compounds are desirably used in an amount in terms of aluminum atom in present in the reaction system of aluminum atom to 10^{-4} to 10^{-1} gram atom/l, preferably 5×10^{-4} to 5×10^{-2} gram atom/l.

The polymerization temperature employed is from −50° to 150° C., preferably from 0° to 120° C.

The olefin polymerization mentioned above is carried out usually in vapor phase or liquid phase. In the liquid phase polymerization, the solvent used may be inert hydrocarbon, or the olefin itself may also be used as the solvent.

The hydrocarbon used in that case includes aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, heptane, octane, decane, dodecane, hexadecane and octadecane, alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane and cyclooctane, aromatic hydrocarbons such as benzene, toluene and xylene, and petroleum fractions such as gasoline, kerosine and gas oil.

The polymerization pressure employed is usually from ordinary pressure to 100 kg/cm^2, preferably from ordinary pressure to 50 kg/cm^2, and the polymerization may be carried out batchwise, semi-continuously or

continuously. A molecular weight of the resulting polymer may be modified by the addition of hydrogen and/or by regulation of the polymerization temperature employed.

Hereinafter, the first propylene/α-olefin random copolymers and process for preparing the same of the present invention are illustrated in detail.

The propylene/α-olefin random copolymers of the present invention are random copolymers of propylene and α-olefins of 4~20 carbon atoms. The propylene/α-olefin random copolymers of the invention desirably contain structural units (a) derived from propylene in an amount of 90 99 mol%, preferably 92~98 mol%, and structural units (b) derived from α-olefin in an amount of, 1~10 mol%, preferably 2~8 mol%. When the structural units (a) derived from propylene contained in the propylene/α-olefin random copolymer are less than 90 mol%, said copolymer tends to become poor in anti-blocking properties and stiffness and, on the other hand, when said units (a) are in excess of 99 mol%, said copolymer tends to increase in melting point and become poor in heat-sealing properties.

α-olefins of 4~20 carbon atoms used herein include 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octane, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Among these, particularly preferred is 1-butene.

The propylene/olefin random copolymers of the present invention desirably have an intrinsic viscosity [η]of 0.5~6 dl/g, preferably 1~5 dl/g as measured in decalin at 135° C. If this intrinsic viscosity is less than 0.5 dl/g, the copolymers tend to become poor in anti-blocking properties and toughness and, on the other hand if said intrinsic viscosity exceeds 6 dl/g, the copolymers tend to become port in moldability.

Further, the propylene/α-olefin random copolymers of the invention have a melting point [Tm] as measured by a differential scanning calorimeter falling within the range of

$$90 < Tm < 155 - 3.5\,(100 - P), \text{ preferably}$$

$$100 < Tm < 150 - 3.5\,(100 - P)$$

wherein P is the content (mol%) of propylene in the copolymer.

In FIG. 2, there is shown as a straight line A the schematic relationship between the melting point Tm of the above-mentioned propylene/α-olefin random copolymer and the propylene content (mol%) present in said copolymer. In this FIG. 2, there is also shown as a straight line B the relationship between the melting point Tm of the known propylene/α-olefin random copolymer and the propylene content (mol%) present in said copolymer.

As is clear from FIG. 2, the melting point of the first propylene/α-olefin random copolymers of the present invention is lower by 10~20° C. than that of the known propylene/α-olefin random copolymers when the amount of α-olefin copolymerized of the former is the same as that of the latter. Accordingly, films obtained from the first propylene/α-olefin random copolymers of the invention are excellent particularly in heat-sealing properties at low temperatures, and the films exhibit excellent heat-sealing properties even when they have small amounts of the copolymerized α-olefin, and hence they are excellent in anti-blocking properties and have excellent stiffness.

In the present invention, the propylene/α-olefin random copolymer was allowed to stand in a differential scanning calorimeter (DSC) at 200° C. for 5 minutes, cooled up to 20° C. at a rate of 10° C./min, and allowed to stand at 20° C. for 5 minutes, and then the temperature was elevated from 20° C. to 200° C. at a rate of 10° C./min to obtain a temperature (Tm) at a maximum endothermic peak which was then taken as a melting point of said propylene/α-olefin random copolymer.

The molecular weight distribution ($\overline{M}w/\overline{M}n$) of the first propylene/α-olefin random copolymers of the invention as obtained by gel permeation chromatography (GPC) is less than 3.5, preferably less than 3.0 and especially less than 2.5. As stated above, the first propylene/α-olefin random copolymers of the invention are narrow in molecular weight distribution and, from this point, they have excellent anti-blocking properties.

The determination of melting point was conducted by using about 2.5 mg of the specimen and DSC of Perkin Elmer-7 Model at heat-up rate of 10° C./min.

The first propylene/α-olefin random copolymers of the invention are desirably to have a soluble portion in boiling n-pentane in an amount of less than 3% by weight, preferably less than 2% by weight and especially less than 1% by weight.

Further, the first propylene/α-olefin random copolymers of the invention are desirably to have an insoluble portion in boiling trichloroethylene in an amount of less than 5% by weight, preferably less than 3% by weight and especially less than 1% by weight.

The amounts of the insoluble portion in boiling trichloroethylene and the soluble portion in boiling n-pentane were determined by such a manner that about 3 g of the finely pulverized specimen was extracted for 5 hours with 180 ml of each of the solvents in a cylindrical filter paper by using a Soxhlet's extractor, and the extraction residue was dried with a vacuum dryer until it reached a constant weight to obtain the weight thereof, whereby a difference in weight between the dried residue and the original specimen is calculated.

The first propylene/α-olefin random copolymers of the present invention as illustrated above may be prepared by copolymerizing propylene and α-olefin of 4~20 carbon atoms at a temperature of 40°~100° C. so that the structural units (a) derived from propylene are present in an amount of 90~99 mol% and the structural units (b) derived from α-olefin are present in an amount of 1~10 mol%, in the presence of catalysts formed from

[A] hafnium compounds having as ligands multidentate compounds in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups, and

[B] organoaluminum oxy-compounds.

In that case, the copolymerization may be carried out by employing the same conditions as used in the preparation of the aforementioned ethylene copolymers.

The first propylene/α-olefin random copolymers of the present invention are excellent particularly in heat-sealing properties at low temperatures and hence are used as heat-sealing agents.

Hereinafter, the second propylene random copolymers and process for preparing the same of the present invention are illustrated in detail.

The second propylene random copolymers of the invention are random copolymers of propylene, ethylene and α-olefins of 4~20 carbon atoms. In the propy-

lene random copolymers, the structural units (a) derived from propylene are present in an amount of 90□99 mol%, preferably 92~98 mol%, the structural units (b) derived from ethylene in an amount of 0.5~9.5 mol%, preferably 1~9 mol%, and the structural units (c) derived from α-olefin in an amount of 0.5~9.5 mol%, preferably 1~9 mol%. If the structural units (a) derived from propylene present in the said copolymers are less than 90 mol%, the copolymers tend to become poor in anti-blocking properties and stiffness. On the other hand, if the structural units (a) exceed 99 mol%, the copolymers tend to increase in melting point and become poor in heat-sealing properties.

α-olefins of 4~20 carbon atoms used herein include 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octane, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Among these, particularly preferred is 1-butene.

The second propylene random copolymers of the invention desirably have an intrinsic viscosity [η] as measured in decalin at 135° C. of 0.5~6 dl/g, preferably 1~5 dl/g. If this intrinsic viscosity is less than 0.5 dl/g, the copolymers tend to become poor in anti-blocking properties and toughness and, on the other hand, if said intrinsic viscosity exceeds 6 dl/g, the copolymers tend to become poor in moldability.

Further, the second propylene/α-olefin random copolymers of the invention have a melting point [Tm]as measured by a differential scanning calorimeter falling within the range of

$$70<Tm<155-5.5\,(100-P),\ \text{preferably}$$

$$90<Tm<150-5.5\,(100-P)$$

wherein P is the content (mol%) of propylene in the copolymer.

The schematic relationship between the melting point Tm of the above-mentioned propylene random copolymer and the propylene content (mol%) in said copolymer is the same as shown in FIG. 2.

In this manner, the melting point of the second propylene random copolymers is lower by 10°~20° C. than that of the known propylene/α-olefin random copolymers when the amounts of ethylene and α-olefin copolymerized of the former are the same as those of the latter. Accordingly, films obtained from the second propylene random copolymers of the invention are excellent particularly in heat-sealing properties at low temperatures, and the films exhibit excellent heat-sealing properties even when they have small amounts of ethylene and α-olefin copolymerized, and hence they are excellent in anti-blocking properties and have excellent stiffness.

Further, the molecular weight distribution $\overline{M}w/\overline{M}n$) of the second propylene random copolymers of the invention as obtained by gel permeation chromatography (GPC) is less than 3.5, preferably less than 3.0 and especially less than 2.5. As stated above, the second propylene random copolymers of the invention are narrow in molecular weight distribution and, from this point, they have excellent anti-blocking properties.

The second propylene random copolymers of the invention are desirably to have a soluble portion in boiling n-pentane in an amount of less than 5% by weight, preferably less than 3% by weight and especially less than 2% by weight.

Furthermore, the second propylene random copolymers of the invention are desirably to have an insoluble portion in boiling trichloroethylene in an amount of less than 5% by weight, preferably less than 3% by weight and especially less than 1% by weight.

The second propylene random copolymers of the present invention as illustrated above may be prepared by copolymerizing propylene, ethylene and α-olefins of 4~20 carbon atoms at a temperature of 40°~100° C. so that the structural units (a) derived from propylene are present in an amount of 90~99 mol% in the resulting copolymers, the structural units (b) derived from ethylene in an amount of 0.5~9.5 mol%, and the structural units (c) derived from α-olefin in an amount of 0.5~9.5 mol%, in the presence of catalysts formed from

[A] hafnium compounds having as ligands multidentate compounds in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups, and

[B] organoaluminum oxy-compounds.

In that case, the copolymerization may be carried out by employing the same conditions as used in the preparation of the aforementioned ethylene copolymers.

The second propylene random copolymers of the invention as illustrated above are excellent particularly in heat-sealing properties at low temperatures, and hence are used as heat-sealing agents.

Hereinafter, the first olefin polymerization catalysts of the present invention are illustrated in detail.

The first olefin polymerization catalysts of the invention are formed from

[A] hafnium compounds having as ligands multidentate compounds in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups,

[B] organoaluminum oxy-compounds, and

[C] organoaluminum compounds.

In the olefin polymerization catalyst mentioned above, the hafnium compounds [A]and organoaluminum oxy-compounds [B]used may be the same as those mentioned previously.

The organoaluminum compounds [C] used herein may be those having in the molecule at least one Al-C bond, for example, the compounds as mentioned below.

That is, (i) organoaluminum compounds represented by the general formula $(R^1)_mAl(OR^2)_nH_pX_q$ wherein R^1 and R^2, which may be the same or different, are each hydrocarbon of usually 1 to 15 carbon atoms, preferably 1 to 10 carbon atoms, X is halogen, m is $1 \leqq m \leqq 3$, n is $0 \leqq n \leqq 2$, p is $0 \leqq p \leqq 2$, and q is $0 \leqq q \leqq 2$, and $m+n+p+q=3$, and (ii) alkylated complex compounds of metals of Group 1 of the periodic table and aluminum represented by the general formula $M_1^4(R^1)_4$ wherein M^1 is Li, Na or K, and R^1 is as defined above.

Of the organoaluminum compounds mentioned above, particularly preferred are those having hydrocarbon groups other than n-alkyl group. Hydrocarbon groups other than n-alkyl group may include alkyl having a branched chain such as isoalkyl, cycloalkyl and aryl. The organoaluminum compounds as illustrated above may include, for example, trialkylaluminum such as triisopropylaluminum, triisobutylaluminum, tri-2-methylbutylaluminum, tri-3-methylbutylaluminum, tri-2-methylpentylaluminum, tri-3-methylpentylaluminum, tri-4-methylpentylaluminum, tri-2-methylhexylaluminum, tri-3-methylhexylaluminum and tri-2-ethylhexylaluminum; tricycloalkylaluminum such as

tricyclohexylaluminum; triarylaluminum such as triphenylaluminum and tritolylaluminum; dialkylaluminum hydrides such as diisobutylaluminum hydride; and alkylaluminum alkoxides such as isobutylaluminum methoxide, isobutylaluminum ethoxide and isobutylaluminum isopropoxide. Of these organoaluminum compounds, preferred are those having branched alkyl groups, particularly trialkylaluminum compounds. Furthermore, isoprenylaluminum represented by the general formula $(i\text{-}C_5H_9)_xAl_y(C_5H_{10})_z$ wherein x, y and z are each a positive integer, and $z \geqq 2x$, is also useful. Compounds capable of forming the above-mentioned organoaluminum compounds in the polymerization system, for example, halogenated aluminum and alkyl lithium, or halogenated aluminum and alkyl megnesium, may be added to the polymerization system.

In polymerizing olefin by using the first olefin polymerization catalysts of the present invention, the hafnium compound [A] is desirably used in an amount, in terms of hafnium atoms present in the polymerization reaction system, of $10^{-8}\sim10^{-2}$ gram atom/l, preferably $10^{-7}\sim10^{-3}$ gram atom/l, the organoaluminum oxy-compound [B] is desirably used in an amount, in terms of aluminum atoms present in the polymerization reaction system, of less than 3 mg atom/l, preferably 0.01~2 mg atom/l and especially 0.02~1 mg atom/l, and the organoaluminum compound [C] is desirably used in such an amount that the proportion of aluminum atoms derived from said organoaluminum compound [C] in the reaction system to the total aluminum atoms of the organoaluminum oxy-compound [B] and organoaluminum compound [C] is 20~99%, preferably 25~98% and especially 30~95%.

In the reaction system, the ratio of the total aluminum atom of the organoaluminum oxy-compound [B] and organoaluminum compound [C] to halfnium atoms of the hafnium compound [A] is usually 20~10000, preferably 50~5000 and especially 100~2000.

The olefin polymerization may be carried out by employing the same condition as used in the preparation of ethylene copolymers as aforesaid.

Hereinafter, the second olefin polymerization catalysts of the present invention are illustrated in detail.

The second olefin polymerization catalysts of the invention are formed from

[A] hafnium compounds having as ligands multidentate compounds in which at least two groups selected from among conjugated cycloalkadienyl groups or substituted groups thereof are linked together via lower alkylene groups,

[B-1] organoaluminum oxy-compounds formed from tri-n-alkylaluminum, and

[B-2] organoaluminum oxy-compounds in which at least one hydrocarbon group other than n-alkyl is linked to Al atom.

In the olefin polymerization catalysts mentioned above, the hafnium compounds [A] used are the same as those mentioned previously.

The catalyst components [B-1] used in the second olefin polymerization catalysts of the invention are organoaluminum oxy-compounds formed from tri-n-alkylaluminum.

n-alkyl group in the tri-n-alkylaluminum mentioned above includes methyl, ethyl, n-propyl, n-butyl, n-octyl and n-decyl. Among these, particularly preferred is methyl.

The catalyst components [B-2] used in the second olefin polymerization catalysts of the invention are organoaluminum oxy-compounds in which at least one hydrocarbon group other than n-alkyl is linked to Al atom.

The hydrocarbon group other than n-alkyl includes alkyl having branched chain such as isoalkyl, cycloalkyl and aryl.

The above-mentioned organoaluminum oxy-compounds [B-2] in which at least one hydrocarbon group other than n-alkyl is linked to Al atom may be formed from organoaluminum compounds in which at least one hydrocarbon group other than n-alkyl is linked to Al atom. Such organoaluminum compounds as used in the above case include, for example, trialkylaluminum such as triisopropylaluminum, triisobutylauminum, tri-2-methylbutylaluminum, tri-3-methylbutylaluminum, tri-2-methylpentylaluminum, tri-3-methylpentylaluminum, tri-4-methylpentylaluminum, tri-2-methylhexylaluminum, tri-3-methylhexylaluminum and tri-2-ethylhexylaluminum; tricycloalkylaluminum such as tricyclohexylaluminum; triarylaluminum such as triphenylaluminum and tritolylaluminum; dialkylaluminum hydrides such as diisobutylaluminum hydride; and alkylaluminum alkoxides such as isobutylaluminum methoxide, isobutylaluminum ethoxide and isobutylaluminum isopropoxide. Of these organoaluminum compounds, preferred are those having branched alkyl groups, particularly trialkylaluminum compounds. Furthermore, isoprenylaluminum represented by the general formula $(i\text{-}C_4H_9)_xAl_y(C_5H_{10})_z$ wherein x, y and z are each a positive integer, and $z \pm 2x$, is also useful.

In polymerization olefin by using the second olefin polymerization catalysts of the present invention, the hafnium compound [A] is desirably used in an amount, in terms of hafnium atoms present in the polymerization reaction system, of $10^{-8}\sim10^{-2}$ gram atom/l, preferably $10^{-7}\sim10^{-3}$ gram atom/l, the organoaluminum oxy-compound [B-1] in an amount, in terms of aluminum atoms in the polymerization reaction system, of less than 3 mg atom/l, preferably 0.01~2 mg atom/l and especially 0.02~1 mg atom/l, and the organoaluminum oxy-compound [B-2] in such an amount that the proportion of aluminum atoms derived from the organoaluminum oxy-compound [B-2] in the reaction system to the total aluminum atom of the organoaluminum oxy-compound [B-1] and organoaluminum oxy-compound [B-2] is 20~95%, preferably 25~90% and especially 30~85%.

In the reaction system, the ration of the total aluminum atom of the organoaluminum oxy-compound [B-1] and organoaluminum oxy-compound [B-2] to hafnium atoms of the hafnium compound [B] is usually 20~10000, preferably 50~5000 and especially 100~2000.

In that case, the olefin polymerization may be carried out by employing the same conditions as used in the preparation of ethylene copolymers as aforesaid.

EFFECT OF THE INVENTION

Novel ethylene copolymers of the present invention are small in $\overline{M}w/\overline{M}n$ and narrow in molecular weight distribution and, moreover, large in MFR_{10}/MFR_2 and excellent in flowability. Accordingly, the ethylene copolymers of the invention have excellent processability and are excellent in anti-blocking properties and the like properties.

Novel propylene copolymers of the invention are low in melting point in comparison with known propylene-/α-olefin random copolymers even when said novel

propylene copolymers are low in α-olefin content, and hence they have excellent anti-blocking properties and stiffness. In the present invention, there are also provided processes for preparing these novel copolymers mentioned above readily and efficiently.

The olefin polymerization catalysts of the invention exhibit high activities even when relatively small amounts of organoaluminum oxy-compounds are used therein, and by the use of said catalysts, olefin polymers large in molecular weight and narrow in molecular weight distribution and composition distribution are obtained.

The present invention is illustrated below with reference to examples, but it should be construed that the invention is in no way limited to those examples.

EXAMPLE 1

(Preparation of ethylene copolymer)

(Preparation of methylaluminoxane)

Methylaluminoxane was prepared in accordance with the procedure described in Polymer Commun., 29, 180 (1988).

(Synthesis of ethylenebis(indenyl)hafnium dichloride)

A nitrogen-purged 200 ml glass flask was charged with 5.4 g of bis(indenyl)ethane [synthesized on the basis of Bull Soc. Chim., 2954 (1967)] and 50 ml of THF, and the flask was cooled with stirring to −30°–40° C. To the flask was added dropwise 31.5 ml of n-Bu Li (1.6M solution), stirred successively at −30° C. for 1 hours, and the temperature was elevated spontaneously to room temperature, thereby anionizing the bis(indenyl)ethane. Separately, a nitrogen-purged 200 ml glass flask was charged with 60 ml of THF, and the flask was cooled to below −60° C., followed by gradual addition of 6.7 g of $HfCl_4$ (contained 0.78% by weight of zirconium atoms as contaminants). Thereafter, the flask was heated-up to 60° C. and stirred for 1 hour. To the flask was added dropwise the anionized ligand, and stirred at 60° C. for 2 hours, followed by filtration with a glass filter. The filtrate was concentrated at room temperature to about 1/5 of the original volume. By this operation, solids were separated. The separated solids were filtered with a glass filter, followed by washing with hexane/ethyl ether and vacuum drying to obtain ethylenebis(indenyl)hafnium dichloride.

The hafnium compound thus obtained contained 0.40% by weight of zirconium atoms.

(Polymerization)

A thoroughly nitrogen-purged 2 liter glass flask was charged with 950 ml of toluene and 50 ml of 1-octene, and ethylene gas was passed therethrough at a rate of 160 l/hr. The temperature in the system was elevated to 55° C., and 1.88 mmoles in terms of aluminum atom of methylaluminoxane and 7.5×10^{-3} mmole of ethylenebis(indenyl)hafnium dichloride were added to the system to initiate polymerization. The polymerization was carried out at 60° C. for 10 minutes under atmospheric pressure while continuously feeding ethylene gas. The polymerization was stopped by the addition of small amounts of methanol, and the polymerization solution obtained was poured in large amounts of methanol to separate polymer. The separated polymer was dried at 130° C. for 12 hours under reduced pressure to obtain 23.2 g of a polymer having a density of 0.866 g/cm^3, the ethylene content of 81.3 mol%, [η] of 1.71 dl/g, $\overline{M}w/\overline{M}n$ of 2.59, MFR_2 of 2.12 g/10 min and MFR_{10}/MFR_2 ratio of 13.1.

EXAMPLE 2

A thoroughly nitrogen-purged 2 liter glass flask was charged with 1 liter of toluene, and a mixed gas of ethylene and propylene (140 l/hr and 40 l/hr respectively) was passed therethrough. The temperature in the system was elevated to 75° C., and 1.88 mmoles in terms of aluminum atom of methylaluminoxane and 7.5×10^{-3} mmol of ethylenebis(indenyl)hafnium dichloride were added to the system to initiate polymerization. The polymerization was carried out at 80° C. for 10 minutes under atmospheric pressure while continuously feeding the above-mentioned mixed gas to the system. Thereafter, the operation was conducted in the same manner as in Example 1 to obtain 17.5 g of a polymer having a density of 0.887 g/cm^3, the ethylene content of 84.0 mol%, [η] of 1.50 dl/g, $\overline{M}w/\overline{M}n$ of 2.50, MFR_2 of 0.80 g/10 min and MFR_{10}/MFR_2 ratio of 12.7.

COMPARATIVE EXAMPLE 1

A copolymer of ethylene and propylene (prepared by using a catalyst composed of $VOCl_3$ and aluminum ethyl sesquichloride) having a density of 0.87 g/cm^3, MFR_2 of 2.9 g/10 min and $\overline{M}w/\overline{M}n$ of 2.16 was found to have MFR_{10}/MFR_2 ratio of 5.90.

EXAMPLE 3

(Preparation of hafnium catalyst)

A glass column of 35 mm in inside diameter was filled with a suspension in toluene of 40 g of dimethylsilylated silica gel (Art. 7719, a product of MERCK) deaerated at room temperature for 4 hours. Subsequently, 200 ml of the toluene solution (Hf=2.07 mmol/l) of ethylenebis(indenyl)hafnium dichloride prepared in Example 1 was gradually poured into the column. A hafnium solution (Hf=0.17 m mol/l) eluted by this operation was used as a catalyst component.

(Polymerization)

The polymerization was carried out in the same manner as in Example 1 except that the polymerization was carried out at 70° C. for 35 minutes using 6.6×10^{-3} mg atom of hafnium atom, to obtain 42.4 g of a colorless transparent polymer having a density of 0.855 g/cm^3, the ethylene content of 76.2 mol%, [η] of 1.89 dl/g, $\overline{M}w/\overline{M}n$ of 2.48, MFR_2 of 1.49 g/10 min and MFR_{10}/MFR_2 ratio of 10.1.

EXAMPLE 4

The polymerization was carried out in the same manner as in Example 2 except that the hafnium catalyst component prepared in Example 3 was used in an amount of 6.6×10^{-3} mg atom in terms of hafnium atom to obtain 17.0 g of a colorless transparent polymer having a density of 0.883 g/cm^3, the ethylene content of 83.5 mol%, [η] of 1.61 dl/g, $\overline{M}w/\overline{M}n$ of 2.54, MFR_2 of 0.73 g/10 min, and MFR_{10}/MFR_2 ratio of 12.2.

EXAMPLE 5

The polymerization was carried out in the same manner as in Example 1 except that the polymerization temperature employed was 40° C. and the polymerization time employed was 15 minutes to obtain 20.5 g of a polymer having a density of 0.868 g/cm^3, the ethylene

content of 82.0 mol%, [η] of 1.79 dl/g, $\overline{M}w/\overline{M}n$ of 2.81, MFR_2 of 0.90 g/10 min and MFR_{10}/MFR_2 ratio of 32.0.

EXAMPLE 6

Preparation of propylene copolymer)

(Polymerization)

A thoroughly nitrogen-purged 2 liter stainless steel autoclave was charged at room temperature with 500 ml of toluene, 3 moles of propylene, 0.1 mole of 1-butene and 5 mg atom in terms of Al atom of methylaluminoxane. The temperature in the polymerization system was elevated to 45° C., and 1.25×10^{-3} mmole of the ethylenebis(indenyl)hafnium dichloride obtained in Example 1 was added to the system to carry out polymerization at 50° C. for 0.5 hours. The polymerization was stopped by the addition of methanol to the polymerization system.

The polymer slurry obtained was poured into large amounts of methanol, the slurry was recovered by filtration and washed with an isobutyl alcohol/hydrochloric acid solution to remove the catalyst components therefrom. The recovered slurry was then vacuum dried overnight at 80° C. and 200~300 mmHg to obtain 27.5 g of a polymer having the 1-butene content of 2.2 mol%, [η] of 3.02 dl/g as measured in Decalin at 135° C., a melting point of 124° C. as measured by DSC, a boiling trichloroethylene-insoluble content of 0% by weight, boiling n-pentane-soluble content of 0.3% by weight and $\overline{M}w/\overline{M}n$ of 2.41 as measured by GPC.

EXAMPLE 7

The polymerization was carried out in the same manner as in Example 6 except that the amount of 1-butene charged was changed to 0.25 mol to obtain 29.1 g of a polymer having the 1-butene content of 5.6 mol%, [η] of 2.95 dl/g, a melting point of 116° C., a boiling trichloroethylene-insoluble content of 0% by weight, a boiling n-pentane-soluble content of 0.4% by weight and $\overline{M}w/\overline{M}n$ of 2.33.

EXAMPLE 8

(Polymerization)

A mixed gas composed of 96.7 mol% of propylene, 2.1 mol% of 1-butene and 1.2 mol% of ethylene was prepared.

A thoroughly nitrogen-purged 2 liter stainless steel autoclave was charged with 500 ml of toluene and then cooled to 0° C., and the autoclave was further charged with 3 moles of the mixed gas prepared above and 5 mg atom in terms of Al atom of methylaluminoxane. The temperature in the polymerization system was elevated to 45° C., and 1.25×10^{-3} m mole of the ethylenebis(indenyl)hafnium dichloride obtained in Example 1 was added to the system to initiate polymerization at 50° C. for 0.5 hours. The polymerization was stopped by the addition of methanol to the polymerization system. The polymer slurry obtained was poured into large amounts of methanol, the slurry was recovered by filtration and washed with an isobutyl alcohol/hydrochloric acid solution to remove the catalyst components therefrom. The recovered polymer was then vacuum dried overnight at 80° C. and 200~300 mmHg to obtain 51.3 g of a polymer having the 1-butene content of 1.4 mol%, the ethylene content of 1.1 mol%, [η] of 3.32 dl/g as measured in decalin at 135° C., a melting point of 121° C. as measured by DSC, a boiling trichloroethylene-insoluble content of 0% by weight, boiling n-pentane-soluble content of 0.9% by weight and $\overline{M}w/\overline{M}n$ of 2.45 as measured by GPC.

EXAMPLE 9

The polymerization was carried out in the same manner as in Example 8 except that the mixed gas composed of 95.1 mol% of propylene, 3.9 mol% of 1-butene and 1.0 mol% of ethylene was used to obtain 48.5 g of a polymer having the 1-butene content of 2.7 mol%, the ethylene content of 0.8 mol%, [η] of 3.29 dl/g, a melting point of 118° C., a boiling trichloroethylene-insoluble content of 0% by weight, a boiling n-pentane-soluble content of 1.1% by weight and $\overline{M}w/\overline{M}n$ of 2.40.

EXAMPLE 10

(Polymerization)

A thoroughly nitrogen-purged 2 liter stainless steel autoclave was charged with 750 ml of toluene and then saturated with propylene gas. To the autoclave were added 7.5 mg atom in terms of Al atom of methylaluminoxane and 1.88×10^{-3} mmole of the ethylenebis(indenyl)hafnium dichloride. Polymerization was carried out at 50° C. for 0.5 hour at the total pressure of 7 kg/cm² G while continuously feeding propylene gas to the autoclave. The polymerization was stopped by the addition of methanol to the polymerization system. The polymer slurry obtained was poured into large amounts of methanol, the slurry was recovered by filtration and washed with an isobutyl alcohol/hydrochloric acid solution to remove the catalyst components therefrom. The recovered slurry was then vacuum dried overnight at 80° C. and 200~300 mmHg to obtain 107.1 g of an isotactic polypropylene having $\overline{M}w/\overline{M}n$ of 1.89 as measured by GPC, a melting point of 132° C. as measured by DSC, [η] of 2.82 dl/g as measured in Decalin at 135° C., a boiling trichloroethylene-insoluble content of 0% by weight and a boiling n-pentane-soluble content of 0.2% by weight.

EXAMPLE 11

A mixed gas composing 98.5 mol% of propylene gas and 1.5 mol% of ethylene gas was prepared. The operation subsequent thereto was carried out in the same manner as in Example 6 to obtain 53.3 g of a polymer having the ethylene content of 1.3 mol%, [η] of 3.50 dl/g, a melting point of 125° C., a boiling trichloroethylene-insoluble content of 0% by weight, a boiling n-pentane-soluble content of 1.0% by weight and $\overline{M}w/\overline{M}n$ of 2.39.

EVALUATION

Heat-sealing properties of the propylene polymers obtained hereinabove were evaluated in the following manner.

PREPARATION OF FILM

On a press plate were placed an aluminum sheet of a 0.1 mm thick, a polyester sheet (a product sold under a trade name of Rumiler by Toray) and a polyimide resin sheet (a product sold under a trade name of Capton by Du Pont), a square of 15 cm×15 cm of the center of which had been cut off, in that order, and 0.8 g of the specimen was placed in this center (the cut-off portion of the polyimide resin sheet), and then Rumiler ®, an aluminum sheet and a press Plate were superposed thereon in that order (see FIG. 3).

The specimen thus interposed between the press plates was placed in a hot press kept at 200° C. and preheated for about 5 minutes, followed by subjecting three times to pressure application (20 kg/cm² G) and release operation in order to remove air bubbles present in the specimen. Subsequently, the pressure was increased finally to 150 kg/cm² G and the specimen was heated for 5 minutes under pressure. After releasing the pressure, the press plate was taken out from a press machine and transferred to separate press machine kept at 30° C. in its press in portion and then cooled for 4 minutes at a pressure of 100 kg/cm², followed by releasing the pressure and taking out the specimen therefrom. Of the films thus obtained, those having a uniform thickness of 50~70 μm were used as the films for measurement.

Measurement of heat-sealing strength

The films thus prepared are placed for 2 days in a hygrostat kept at 50° C. (aging). In practicing the aging, sheets of paper are applied to both sides of the film so that the films do not come in contact with each other. The films thus aged are cut up into strips of a 15 mm thick, and two sheets of the strip are placed one upon another and then interposed between two sheets of Teflon Film of a 0.1 mm thick, followed by heat sealing. The heat sealing is carried out while maintaining the temperature of a lower portion of a hot plate of heat sealer constant at 70° C. and varying only the temperature of an upper portion of hot plate suitably at intervals of 5° C. The heat-sealing pressure employed is 2 kg/cm², the heat-sealing time employed is 1 second, and a width of heat seal is 5 mm (accordingly a sealed area is 15 mm×5 mm).

Heat-sealing strength is determined by obtaining a peeling strength of the heat sealed film subjected to peeling test at a rate of 30 cm/min at each heat-sealing temperature as mentioned above. (See FIG. 4.)

Following the above-mentioned procedure, a peeling strength at each of the heat-sealing temperatures preset at interval of 5° C. is obtained, and the plots of heat-sealing temperature-peeling strength are connected by means of a curved line. On the basis of the curved line, a heat sealing temperature corresponding to a peeling strength of 800 g /15 mm is taken as a completely heat-sealed temperature (see FIG. 5).

Table 1 below shows completely heat-sealed temperatures of the propylene polymers obtained in the foregoing examples.

TABLE 1

Example	6	7	8	9	10	11
Completely heat-sealed temperature (°C.)	134	125	117	122	120	127

EXAMPLE 12

(Preparation of organoaluminum oxy-compound [B-1])

A thoroughly nitrogen-purged 400 ml flask was charged with 37 g of $Al_2(SO_4)_3 \cdot 14H_2O$ and 125 ml of toluene and cooled to 0° C., followed by dropwise addition of 500 mmol of trimethylaluminum diluted with 125 ml of toluene. The temperature of the flask was elevated to 40° C., and reaction was continued at that temperature for 10 hours. After the completion of the reaction, solid-liquid separation of the reaction mixture was effected by filtration, and the toluene was removed from the filtrate to obtain 13 g of a white solid organoaluminum oxy-compound. The molecular weight of the compound obtained was 930 as measured in benzene by the cryoscopic method, and m value shown in the catalyst component [B-1] was 14.

(Polymerization)

A thoroughly nitrogen-purged 2 liter stainless steel autoclave was charged with 500 ml of toluene, and the system was purged with propylene gas. Successively, to the autoclave were added 1 mmol of triisobutylaluminum, 1 mg atom in terms of Al atom of the organoaluminum oxy-compound obtained above, and 1×10^{-3} mmol of the ethylenebis(indenyl)hafnium dichloride obtained in Example 1, and the temperature of the system was elevated to 45° C. Thereafter, polymerization was carried out at 50° C. for 1 hours, while feeding propylene gas to the polymerization system so that the total pressure became 7 kg/cm² G, to obtain 45.0 g of an isotactic polypropylene having $[\eta]$ of 2.5 dl/g as measured in Decalin at 135° C., $\overline{M}w/\overline{M}n$ of 2.2, a melting point of 132° C., a boiling trichloroethylene-insoluble content of 0% by weight and a boiling n-pentane-soluble content of 0.2% by weight.

COMPARATIVE EXAMPLE 2

The polymerization of Example 12 was repeated except that the triisobutylaluminum was not used to obtain 5.1 g of isotactic polypropylene having $[\eta]$ of 1.9 dl/g, $\overline{M}w/\overline{M}n$ of 2.1 and a melting point of 131° C.

EXAMPLE 13

The polymerization of Example 12 was repeated except that in place of the triisobutylaluminum there were used 1 m mol of tri-2-ethylhexylaluminum and 0.5 mg atom in terms of Al atom of commercially available aluminoxane to obtain 38.2 g of isotactic polypropylene having $[\eta]$ of 2.3 dl/g, $\overline{M}w/\overline{M}n$ of 2.4, a melting point of 131° C., a boiling trichloroethylene-insoluble content of 0% by weight and a boiling n-pentane-soluble content of 0.3% by weight.

EXAMPLE 14

A nitrogen-purged 1 liter glass autoclave was charged with 335 ml of toluene and 15 ml of octene, followed by elevating the temperature of the system to 70° C. while blowing ethylene gas thereinto. Successively, to the autoclave were added 0.4 mmol of triisobutylaluminum, 0.2 mg atom in terms of Al atom of commercially available aluminoxane and 3×10^{-3} mmol of the ethylenebis(indenyl)hafnium dichloride obtained in Example 1 to initiate polymerization. The polymerization was carried out at 70° C. for 30 minutes while continuously feeding ethylene gas to the polymerization system to obtain 16.8 g of an ethylene/1-octene copolymer having $\overline{M}w/\overline{M}n$ of 3.18, MFR_2 of 0.09 g/10 min, MFR_{10}/MFR_2 of 30.7 and a density of 0.879 g/cm³.

EXAMPLE 15

(Preparation of organoaluminum oxy-compound [B-2])

A thoroughly nitrogen-purged 400 ml flask was charged with 4.9 g of $Al_2(SO_4)_3 \cdot 14H_2O$ and 125 ml of toluene and cooled to 0° C., followed by dropwise addition of 200 mmol of triisobutylaluminum diluted with 125 ml of toluene. The temperature of the reaction system was elevated to 40° C., and reaction was continued at that temperature for 24 hours. After the completion of the reaction, solid-liquid separation of the reac-

tion mixture was conducted by filtration, the toluene was removed from the filtrate, and a molecular weight of the organoaluminum oxy-compound [B-2] obtained was measured in benzene by the cryoscopic method to find that it was 610.

(Polymerization)

A thoroughly nitrogen-purged 2 liter stainless steel autoclave was charged with 500 ml of toluene, and the system was then purged with propylene gas. Successively, to the autoclave were added 1 mg atom each in terms of Al atom of the organoaluminum oxy-compound [B-1] and the organoaluminum oxy-compound [B-2] and 1.0×10^{-3} mmol of ethylenebis(indenyl)hafnium dichloride, and the temperature of the polymerization system was elevated to 30° C. Thereafter, polymerization was carried out at 30° C. for 20 minutes while feeding propylene gas to the total pressure became 5 kg/cm² G to obtain 9.5 g of isotactic polypropylene having [η] of 4.1 dl/g, $\overline{M}w/\overline{M}n$ of 3.5, a melting point of 135° C., a boiling trichloroethylene-insoluble content of 0% by weight and a boiling n-pentane-soluble content of 0.2% by weight.

EXAMPLE 16

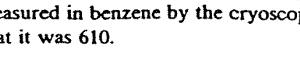
Example 12 was repeated except that the polymerization was carried out under the total pressure of 7 kg/cm²G at 50° C. for 1 hours using 1 mg atom in terms of Al atom of $(iso\text{-}C_4H_9)_2Al\text{-}O\text{-}Al(iso\text{-}C_4H_9)_2$ as the organoaluminum oxy-compound [B-2] and 0.5 mg atom in terms of Al atom of the organoaluminum oxy-compound [B-1] to obtain 35.1 g of isotactic polypropylene having [η] of 2.2 dl/g, Mw/Mn of 2.1, a melting point of 132° C., a boiling trichloroethylene-insoluble content of 0% by weight and a boiling n-pentane-soluble content of 0.3% by weight.

COMPARATIVE EXAMPLE 3

Example 16 was repeated except that the organoaluminum oxy-compound [B 2] was not used to obtain 2.4 g of isotactic polypropylene having [η] of 1.5 dl/g and a melting point of 130° C.

EXAMPLE 17

A thoroughly nitrogen-purged 1 liter glass autoclave was charged with 328 ml of toluene and 22 ml of 1-octene, and the system was then elevated in temperature to 70° C. while blowing ethylene gas thereinto. Successively, to the autoclave were added 0.4 mg atom in terms of Al atom of $(iso\text{-}C_4H_9)_2Al\text{-}(O$



as the organoaluminum oxy-compound [B-2], 0.2 mg atom in terms of Al atom of the above-mentioned organoaluminum oxy-compound [B-1] and 3×10^{-3} mmol of ethylenebis(indenyl)hafnium dichloride to initiate polymerization. The polymerization was carried out at 70° C. for 30 minutes while continuously feeding ethylene gas to the polymerization system to obtain 12.3 g of an ethylene/1-octene copolymer having $\overline{M}w/\overline{M}n$ of 2.49, MFR_2 of 7.2 g/10 min, MFR_{10}/MFR_2 of 9.3 and a density of 0.853 g/cm³.

What is claimed is:

1. In ethylene random copolymers composed of structural units (a) derived from ethylene and structural units (b) derived from α-olefin of 3 to 20 carbon atoms, the improvement which resides in that the ethylene copolymers have

(A) a density of 0.85 to 0.91 g/cm³,

(B) an intrinsic viscosity as measured in decahydronaphthalene at 135° C. of 0.1 to 10 dl/g,

(C) a ratio ($\overline{M}w/\overline{M}n$) of a weight average molecule weight ($\overline{M}w$) to a number average molecular weight ($\overline{M}n$) as measured by PGC of 1.4 to 3.5, and

(D) a ratio (MFR_{10}/MFR_2) of MFR_{10} under a load of 10 kg to MFR_2 under a load of 2.16 kg at 190° C. of 8.5 to 45.

2. The ethylene copolymer of claim 1 wherein said copolymer has density of 0.85–0.90 g/cm³.

3. The ethylene copolymers of claim 1 comprising

(a) 60–96 mol% of structural units derived from ethylene and

(b) 4–40 mol% of structural units derived from α-olefin containing 3–20 carbon atoms.

4. The ethylene copolymers of claim 1 wherein (a) 70–94 mol% of the structural units are derived from ethylene and (b) 6–30 mol% of structural units are derived from α-olefin containing 3–20 carbon atoms.

5. The ethylene copolymers of claim 1 wherein the intrinsic viscosity (η) as measured in decahydronaphthalene at 135° C. is 05–6 dl/g.

6. The ethylene copolymers of claim 1 wherein the molecular weight distribution $\overline{M}w/\overline{M}n$ as measured by GPC is 1.5 to 3.0.

7. The ethylene copolymers of claim 1 wherein the ratio MFR_{10}/MFR_2 is 9 to 40.

* * * * *