EXHIBIT V

PART 4

in small quantities as long as the scope of this invention is kept.

Next, the definitions of physical and chemical properties used in this invention are explained below.

(1) Intrinsic viscosity

This implies [η] in tetralin of 135° C.

$$[\eta] = 11.65 \times \log R$$

$$R = t/t_0$$

t: Seconds of dropping in a concentration of 0.2 dl/g

t_0: Seconds of dropping of tetralin itself

(2) Density

According to the specification in JIS-K-6760.

With respect to the copolymer B of lower molecular weight, when it has a large S.C.B., it is regarded as a low density product, and according to the specification, it must be subjected to annealing of 100° C. and 1 hour. However, the copolymer B was conformed in all cases to the specification for high density products and was not subjected to the above annealing.

(3) S.C.B.

Using the C_{14} labelled product described in the following literature, the subject property was calculated by employing the FT-IR spectrum substraction method.

"Characterization and Properties of Polymers"
Published by KAGAKU DOJIN
Compiled by Mitsuru Nagasawa et al.
Issued on July 10, 1970
Pages 131 to 146

Determination formulas for various branches are given below.

Branch	Determination formula
Methyl	Branches/1000 C = 0.49 · K 7.25μ
Ethyl	Branches/1000 C = 0.70 · K 7.25μ
n-Butyl	Branches/1000 C = 0.80 · K 7.25μ
n-Decyl	Branches/1000 C = 0.78 · K 7.25μ
Other linear chains	Branches/1000 C = 0.80 · K 7.25μ
i-Butyl	Branches/1000 C = 0.45 · K 7.25μ

$K_{7.25\mu}$ (absorptivity) was obtained by using as a reference a linear ethylene homopolymer having the almost same molecular weight and molecular weight distribution and the same [η] as those of a given sample and employing the spectrum substraction method. Therefore, effects of methyl groups at the ends were cleared.

When R of an α-olefin R—CH=CH_2 is a linear alkyl, (the number of methyl groups at the branch ends)/1000C is S.C.B. When R is a branched alkyl group, for instance, an α-olefin is 4-methyl-pentene-1, the branch is the i-butyl group and half number of methyl groups at the branch ends per 1000 carbon atoms is S.C.B.

(4) Weight average molecular weight by light scattering method

This item was measured at 125° C. by the normal method, with α-chloronaphthalin used as a solvent and employing a photoelectric type light scattering photometer (manufactured by SHIMAZU SEISAKUSHO).

(5) Melt index (MI)

According to the condition E of ASTM D 1238.

(6) Melt flow ratio (MFR)

Firstly, $MI_{21.6}$ (grams per 10 min. under a load of 21.6 kg at 190° C.) is measured according to ASTM D 1238 condition F. Then, MFR is calculated using the following formula.

$$MFR = MI_{21.6}/MI$$

(7) Rigidity (expressed by Olsen's flexural modulus)

According to ASTM D 747.

Press condition: ASTM D 1898 method C

Test piece: 25×70×1 mm thickness

Span: 25 mm

Measurement temperature: 20° C.

(8) Tensile impact strength: According to ASTM D 1822

Press condition: ASTM D 1898 method C

Test piece: S type dumbbell, 1 mm thickness

Annealing: 1 hour in boiling water

Measurement temperature: 20° C.

(9) Molecular weight distribution (Mw/Mn)

GPC method (gel permeation chromatography method)

HLC-811 (manufactured by TOYO SODA)

Column: TSK-GEL (GMSP+$G_{7000}H_4$+GMHx2)

Solvent: 1,2,4-trichlorobenzene (TCB)

Temperature: 145° C.

Detector: Differential refractometer

Flow quantity: 1 ml/min.

Concentration: 15 mg/10 ml TCB

Measurement data on standard polystyrenes are shown below.

Polystyrene	Nominal value $\overline{Mw}$	Nominal value $\overline{Mn}$	Nominal value $\overline{Mw}/\overline{Mn}$	Measured value $\overline{Aw}$	Measured value $\overline{An}$	Measured value $\overline{Aw}/\overline{An}$
#41955 (Waters')	9.82×10^4	9.62×10^4	1.02	2083	1744	1.19
A 5000 (TOYO SODA's)	6.2×10^3	5.96×10^3	1.04	140	112	1.25

(10) Environmental stress cracking resistance (ESCR)

According to ASTM D 1693.

Expressed in F_{50} (hr).

The following exceptions were adopted.

Concentration of Antarox-CO630: 10% by weight

Sample: 3 mm thickness, 0.5 mm notch

(11) Tensile strength

According to ASTM D 638.

(12) Resistance to chlorine water

Test solution: 0.2% chlorine water

Solution quantity: A quantity which gives 1.2 ml/cm^2 against a pressed sample. The solution is replaced daily.

Temperature: 40° C.

Evaluation: 10 stage evaluation on a sample after 72 hours.

1: Excellent,

10: Overall surface like "foam"

(13) Transparency (haze value)

Press condition: 180° C.×10 min, rapid cooling in ice water

Sample: 100μ thickness

Haze measurement: Internal haza
(14) Brabender torque
Brabender plastograph ® was used.
Jacket: W 50 model, 45 g filled
Temperature: 190° C.
Rotor revolution: 60 rpm
A torque after 30 min. is expressed in kg-m.
(15) Spiral flow length
Injection molding machine: 5 ounce injection molding machine manufactured by the Japan Steel Works, Ltd.
Mold: Spiral mold (7.5 mmϕ semicircle, 2000 mm length)
Molding condition:
Resin temperature 250° C.
Mold temperature 40° C.
Injection pressure 840 kg/cm²

Injection molding is carried out with this molding condition and spiral flow length is measured.

The present invention is explained below in more detail by the following examples, but it is not restricted by these examples.

EXAMPLE 1

(1) Synthesis of Organomagnesium Compound

In a 500 ml four-necked flask equipped with a stirrer, a reflux condenser, and a dropping funnel was placed 16.0 g of flake-shaped magnesium to be used for the production of Grignard reagents. The air and moisture inside the flask were completely replaced by nitrogen. Into the dropping funnel were charged 68 ml (0.65 mol) of n-butyl chloride and 30 ml of n-butyl ether. About 30 ml of this solution was dropped into the flask to initiate a reaction, and thereafter the rest of the solution was dropped in 4 hours at 50° C. After the completion of dropping, the reaction was continued for further 1.5 hours at 60° C. Then, the reaction system was cooled to room temperature and the unreacted magnesium was filtered off by the use of a glass filter.

n-Butyl magnesium chloride in the n-butyl ether was measured for its concentration by hydrolyzing with 1 N sulfuric acid and back-titrating with 1 N sodium hydroxide using phenolphthalein as an indicator. The concentration was 1.96 mol/l.

(2) Synthesis of Solid Catalyst Component

The air and moisture inside a 500 ml four-necked flask equipped with a stirrer, a dropping funnel and a thermometer was completely replaced by nitrogen. In the flask was placed 130 ml of the n-butyl ether solution containing 0.26 mol of n-butyl magnesium chloride synthesized in the above step (1). From the dropping funnel was dropped 30 ml (0.26 mol) of silicon tetrachloride over 2 hours at 50° C. The reaction was continued further for 1 hour at 60° C. The formed white solid was separated, washed with n-heptane and dried under reduced pressure to obtain 31.5 g of a white solid. Ten grams of this white solid was placed in a 100 ml four-necked flask and 50 ml of titanium tetrachloride was added. They were allowed to react with stirring for 1 hour at 100° C. After the completion of the reaction, n-heptane washing was applied until the washings became free from titanium tetrachloride. After drying under reduced pressure, 7.9 g of a solid catalyst component was obtained. Each 1 g of this solid catalyst component supported 14 mg of titanium.

EXAMPLE 2

Ethylene-α-olefin copolymers A were polymerized, using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing various α-olefins and other polymerization conditions as shown in Table 1. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these polymers obtained were also shown in Table 1.

These copolymers are used in the following examples as mixing components.

EXAMPLE 3

Ethylene-α-olefin copolymers B were polymerized, using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing various α-olefins and other polymerization conditions as shown in Table 2. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these ethylene-α-olefin copolymers were also shown in Table 2.

These copolymers are used in following examples as mixing components.

TABLE 1

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (kg/cm²)	C'_2-partial pressure (kg/cm²)	Polymerization temperature (°C.)	Properties: Density (g/cm³)	Properties: [η] (dl/g)	Properties: S.C.B.	Properties: $\overline{Mw}/\overline{Mn}$
A1-1	Slurry	65	134	TEA 100	C_4 6.0	C'_4 6.14	0.84	5.6	50	0.900	2.2	38	5.9
A1-2	Solution	1	25.3	DEAC 2.5	C_7 0.25	4-MP-1 0.110	0.1	20	140	0.904	2.5	23	3.6
A1-3	Slurry	65	130	TEA 50	C_4 6.0	C'_4 6.14	0.25	6.0	50	0.905	3.2	30	5.8
A1-4	Slurry	65	310	TEA 100	C_4 6.0	C'_4 6.14	0.86	9.5	50	0.915	2.5	19	5.5
A1-5	Slurry	65	102	TEA 50	C_4 6.0	C'_4 6.14	0.059	4.5	50	0.908	4.4	25	6.0
A1-6	Solution	1	26.0	DEAC 2.5	C_7 0.30	C'_6 0.060	0.1	20	140	0.903	2.5	25	3.7
A1-7	Solution	1	327	TEA 100	C_7 0.30	C'_6 0.060	1.8	12.0	140	0.922	2.2	13	5.3
A1-8	Solution	1	24.5	DEAC 2.5	C_7 0.30	4-MP-1 0.050	0.15	20	140	0.920	2.5	10	3.7
A1-9	Slurry	65	330	TEA 100	C_4 6.0	C'_4 6.14	1.1	12.0	50	0.921	2.5	13.	5.5
A1-10	Slurry	65	309	TEA 100	C_4 6.0	C'_4 6.14	1.2	8.0	50	0.911	2.2	25	5.7
A1-11	Slurry	65	121	TEA 50	C_4 6.0	C'_4 6.14	0.98	6.5	50	0.907	2.2	30	5.7
A1-12	Slurry	65	320	TEA 100	C_4 6.0	C'_4 6.14	3.0	20	50	0.928	2.2	8	5.3
A1-13	Solution	1	25.0	DEAC 2.5	C_7 0.25	C'_8	0.1	20	140	0.903	2.5	24	3.9

TABLE 1-continued

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (kg/cm²)	C'_2-partial pressure (kg/cm²)	Polymerization temperature (°C.)	Properties: Density (g/cm³)	[η] (dl/g)	S.C.B.	$\overline{Mw}/\overline{Mn}$
						0.140							

Note
TEA = Triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1: 4-Methylpentene-1
C_2 = Ethylene
C_4 = n-Butane
C'_4 = Butene-1
C'_6 = Hexene-1
C'_8 = Octene-1
C_7 = n-Heptane

TABLE 2

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (kg/cm²)	C'_2 partial pressure (kg/cm²)	Polymerization temperature (°C.)	Properties: Density (g/cm³)	[η] (dl/g)	S.C.B.	$\overline{Mw}/\overline{Mn}$
B1-1	Slurry	65	345	TEA 100	C_4 15.2	C'_4 1.2	11.5	5.0	70	0.943	0.63	15	5.5
B1-2	Solution	1	25.5	DEAC 2.5	C_7 0.28	4-MP-1 0.030	3.0	10	140	0.938	0.50	13	3.5
B1-3	Slurry	65	415	TEA 50	C_4 15.2	C'_4 1.6	11.0	5.0	70	0.936	0.62	20	5.6
B1-4	Slurry	65	425	TEA 50	C_4 15.2	C'_4 2.0	10.5	5.0	70	0.929	0.65	25	5.7
B1-5	Slurry	65	286	TEA 50	C_4 6.0	C'_4 6.14	9.4	8.5	50	0.927	1.1	25	5.8
B1-6	Slurry	65	410	TEA 100	C_4 12.0	C'_4 3.0	11.0	3.0	50	0.910	0.60	35	5.9
B1-7	Solution	1	25.7	DEAC 2.5	C_7 0.25	4-MP-1 0.050	2.5	10	140	0.912	0.52	22	3.6
B1-8	Slurry	65	250	TEA 100	C_4 15.2	C'_4 0.4	13.5	1.5	50	0.930	0.28	25	5.7
B1-9	Slurry	65	407	TEA 100	C_4 15.2	C'_4 0.5	13.0	5.0	70	0.954	0.62	8	5.2
B1-10	Slurry	65	422	TEA 50	C_4 15.2	C'_4 1.8	11.0	5.0	70	0.934	0.61	22	5.6
B1-11	Slurry	65	405	TEA 50	C_4 15.2	C'_4 1.4	11.0	5.0	70	0.939	0.62	18	5.5
B1-12	Solution	1	25	DEAC 2.5	C_7 0.25	C'_8 0.040	3.0	10	140	0.937	0.49	14	3.6

Note
TEA = Triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1 = 4-Methylpentene-1
C_2 = Ethylene
C_4 = n-Butane
C'_4 = Butene-1
C'_6 = Hexene-1
C'_8 = Octene-1
C_7 = n-Heptane

EXAMPLE 4

Ethylene-α-olefin copolymers A were polymerized, using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing various α-olefins and other polymerization conditions shown in Table 3. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these ethylene/α-olefin copolymers were also shown in Table 3.

These copolymers are used in the following examples as mixing components.

EXAMPLE 5

Ethylene-α-olefin copolymers B were polymerized, using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing various α-olefins and other polymerization conditions as shown in Table 4. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these ethylene/α-olefin copolymers were also shown in Table 4.

These copolymers are used in the following examples as mixing components.

TABLE 3

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (kg/cm²)	C'_2-partial pressure (kg/cm²)	Polymerization temperature (°C.)	Properties: Density (g/cm³)	[η] (dl/g)	S.C.B.	$\overline{Mw}/\overline{Mn}$
A2-1	Slurry	65	145	TEA 100	C_4 6.0	C'_4 6.14	1.38	6.0	50	0.902	1.8	38	5.9
A2-2	Solution	1	25.5	DEAC 2.5	C_7 0.25	4-MP-1 0.11	0.5	20	140	0.908	1.8	23	3.8

TABLE 3-continued

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (kg/cm²)	C_2 partial pressure (kg/cm²)	Polymerization temperature (°C.)	Properties: Density (g/cm³)	Properties: [η] (dl/g)	Properties: S.C.B.	Properties: $\overline{M}w/\overline{M}n$
A2-3	Slurry	65	141	TEA 50	C_4 6.0	C'_4 6.14	0.59	6.5	50	0.907	2.5	30	5.8
A2-4	Slurry	65	307	TEA 100	C_4 6.0	C'_4 6.14	2.3	11	50	0.918	1.8	17	5.4
A2-5	Slurry	65	311	TEA 100	C_4 6.0	C'_4 6.14	1.84	8.4	50	0.914	1.8	25	5.7
A2-6	Slurry	65	321	TEA 100	C_4 6.0	C'_4 6.14	3.2	14	50	0.925	1.8	13	5.3
A2-7	Solution	1	26.5	DEAC 2.5	C_7 0.3	4-MP-1 0.05	0.9	20	140	0.923	1.8	10	3.6
A2-8	Slurry	65	315	TEA 100	C_4 6.0	C'_4 6.14	2.6	8.5	50	0.914	1.6	25	5.5
A2-9	Slurry	65	118	TEA 100	C_4 6.0	C'_4 6.14	4.6	17	50	0.929	1.6	10	5.3
A2-10	Solution	1	24.5	DEAC 2.5	C_7 0.3	C'_6 0.025	0.9	20	140	0.918	1.8	13	3.8

Note
TEA = Triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1 = 4-Methylpentene-1
C'_2 = Ethylene
C_4 = n-Butane
C'_4 = Butene-1
C'_6 = Hexene-1
C_7 = n-Heptane

TABLE 4

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (kg/cm²)	C_2 partial pressure (kg/cm²)	Polymerization temperature (°C.)	Properties: Density (g/cm³)	Properties: [η] (dl/g)	Properties: S.C.B.	Properties: $\overline{M}w/\overline{M}n$
B2-1	Slurry	65	348	TEA 100	C_4 15.2	C'_4 1.0	12	3.0	70	0.943	0.51	15	5.9
B2-2	Solution	1	26.5	DEAC 2.5	C_7 0.28	4-MP-1 0.03	3.0	10	140	0.938	0.50	13	3.5
B2-3	Slurry	65	405	TEA 50	C_4 15.2	C'_4 1.6	8.8	5.0	70	0.935	0.73	20	5.9
B2-4	Slurry	65	421	TEA 50	C_4 15.2	C'_4 1.6	12	3.0	70	0.929	0.54	25	5.9
B2-5	Slurry	65	407	TEA 100	C_4 12.0	C'_4 2.5	12	3.0	50	0.910	0.51	35	6.0
B2-6	Solution	1	25.7	DEAC 2.5	C_7 0.25	4-MP-1 0.05	2.5	10	140	0.912	0.52	22	3.6
B2-7	Slurry	65	245	DEAC 2.5	C_4 15.2	C'_4 0.3	12	1.0	50	0.931	0.25	25	5.9
B2-8	Slurry	65	420	TEA 50	C_4 15.2	C'_4 1.2	12	3.0	70	0.938	0.50	18	5.4
B2-9	Solution	1	23.9	DEAC 2.5	C_7 0.30	C'_6 0.017	3.0	10	140	0.937	0.52	18	3.4

Note
TEA = Triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1 = 4-methylpentene-1
C'_2 = Ethylene
C_4 = n-Butane
C'_4 = Butene-1
C'_6 = Hexene-1
C_7 = n-Heptane

EXAMPLE 6

A composition of ethylene-α-olefin copolymers was prepared in two stage polymerization.

The first stage polymerization was carried out for 90 min. by using the catalyst produced in Example 1 and triethyl aluminum (co-catalyst) and employing other polymerization conditions as shown in Table 5. Successively, the second stage polymerization was conducted for 123 min. by changing only the hydrogen partial pressure and the ethylene partial pressure as shown in Table 5. In both polymerization stages, the liquid phase molar ratio of ethylene/butene-1/hydrogen was maintained at respective fixed levels. The polymerized quantities in each stage were examined from the quantities of fed ethylene. The result indicated that the total polymer consisted of about 45% by weight of higher molecular weight components and about 55% by weight of lower molecular weight components. The sample polymer of the former stage was taken out immediately before the completion of the polymerization and was measured for its density, intrinsic viscosity, S.C.B. and (weight average molecular weight/number average molecular weight). Also, similar measurements were made for the whole polymer obtained after the two-stage polymerization. Using the values of the former stage polymer and the whole polymer, the intrinsic viscosity and S.C.B. for the polymer formed in the latter stage alone were calculated. These calculated values are also shown in Table 5. The whole polymer gave: density 0.920 g/cm³, melt index 0.7 g/10 min, melt flow ratio 65, intrinsic viscosity 1.6 dl/g, S.C.B. 25. The whole polymer was measured for its fluidity and solid physical properties. Results are shown in Table 9.

The below-described are mixing methods of an ethylene-α-olefin copolymer A having a relatively higher molecular weight and an ethylene-α-olefin copolymer B having a relatively lower molecular weight.

(a) Mixing with a Banbury mixer (hereinafter referred to as Banbury mixing)

A copolymer A and a copolymer B are mixed in a fixed ratio and in order to give a total quantity of 1.0 kg. The mixture is kneaded in a Banbury mixer for 5 min. with a rotor revolution of 150 to 230 rpm. At that time, nitrogen replacement should be made sufficiently and the polymer temperature must not exceed 250° C.

(b) Mixing in a solution state (hereinafter referred to as solution mixing)

A copolymer A and a copolymer B are mixed in a fixed ratio and in order to give a total quantity of 100 g. This mixture is charged into a 3 liter autoclave. Two liters of xylene is added as a solvent. With stirring, the mixture is heated up to 200° C. and is subjected to 1 hour of solution mixing. Then, it is cooled below the boiling point, and is added into 10 liters of methanol to cause precipitation. The precipitate is dried for 48 hours in a vacuum drier of 80° C. to obtain an intended polymer composition.

EXAMPLE 7

TABLE 5

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	catalyst TEA (=g)	Solvent (g)	α-olefin (g)	H_2 partial pressure (kg/cm²)	C'_2-partial pressure (kg/cm²)	Polymerization temperature (°C.)	Polymerization time (min)	Properties: Density (g/cm³)	Properties: [η] (dl/g)	Properties: S.C.B.	Properties: $\overline{Mw}/\overline{Mn}$
1st stage	Slurry	5	18.5	5	C_4 1000	C'_4 250	0.3	3	50	90	0.902	2.8	35	6.1
2nd stage	Slurry						1.7	8		123	—	(0.62)	(15)	—

Note
C_4 = n-Butane
C'_4 = Butene-1
C'_2 = Ethylene
TEA = Triethyl aluminum
Values in parenthesis are calculated values.

TABLE 6

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst TEA (mg)	Solvent (g)	α-olefin (g)	H_2 partial pressure (kg/cm²)	C'_2-partial pressure (kg/cm²)	Polymerization temperature (°C.)	Polymerization time (min)	Properties: Density (g/cm³)	Properties: [η] (dl/g)	Properties: S.C.B.	Properties: $\overline{Mw}/\overline{Mn}$
1st stage	Slurry	5	25	5	C_4 1000	C'_4 120	0.45	20	50	100	0.910	1.75	30	5.8
2nd stage	Slurry						16	4.0		150	—	(0.5)	(20)	—

Note
C_4 = n-Butane
C'_4 = Butene-1
C'_2 = Ethylene
TEA = Triethyl aluminum
Values in parenthesis are calculated values.

A composition of ethylene-α-olefin copolymers was prepared in two stage polymerization.

The first stage polymerization was carried out for 100 min. by using the catalyst produced in Example 1 and triethyl aluminum (co-catalyst) and employing other polymerization conditions as shown in Table 6. Successively, the second stage polymerization was conducted for 150 min. by changing only the hydrogen partial pressure and the ethylene partial pressure as shown in Table 6. In both polymerization stages, the liquid phase molar ratio of ethylene/butene-1/hydrogen was maintained at respective fixed levels. The polymerized quantities in each stage were examined from the quantities of fed ethylene. The result indicated that the total polymer consisted of about 50% by weight of higher molecular weight components and about 50% by weight of lower molecular weight components. The sample polymer of the former stage was taken out immediately before the completion of the polymerization and was measured for its density, intrinsic viscosity, S.C.B. and (weight average molecular weight/number average molecular weight). Similar measurements were made also for the whole polymer obtained after the two stage polymerization. Using the values of the former stage polymer and the whole polymer, the intrinsic viscosity and S.C.B. for the polymer formed in the latter stage alone were calculated. These calculated values are also shown in Table 6. The whole polymer gave: density 0.923 g/cm³, melt index 6 g/10 min., melt flow ratio 55, intrinsic viscosity 1.10 dl/g, S.C.B. 25. The whole polymer was subjected to injection molding and the molded composition was measured for its physical properties. Results are shown in Table 10.

EXAMPLE 8

The ethylene-α-olefin copolymer A1-1 obtained in Example 2 and the ethylene-α-olefin copolymer B1-1 obtained in Example 3 were mixed at a 50/50 weight ratio and kneaded in a Banbury mixer. A composition having a density, MI and MFR shown in Table 7 was prepared. Physical properties of the composition are also shown in Table 7. For the purpose of comparison, in Table 7 are also shown Comparative example 1 using

a high pressure polyethylene based on the conventional technique (commercial product: Sumikathene ®F101-1 manufactured by Sumitomo Chemical Co., Ltd.) as well as Comparative example 2 using a low density ethylene-α-olefin copolymer of the conventional technique.

As is obvious from Table 7, the polymer composition of this invention is excellent, compared with the high pressure polyethylene, with its lower Brabender torque (excellent in processability) and higher tensile impact strength, ESCR, rigidity and tensile strength.

It is also obvious from Table 7 that, compared with the low density ethylene-α-olefin copolymer of the conventional technique, the polymer composition of this invention has a much lower Brabender torque (very excellent in processability) and a much higher tensile impact strength and tensile strength.

TABLE 7

		Copolymer A		Copolymer B		Properties of composition			
	Mixing method	Designation	% by weight	Designation	% by weight	Density (g/cm³)	MI (g/10 min)	MFR	Distribution index of S.C.B.*
Example 8	Banbury	A1-1	50	B1-1	50	0.921	1.1	65	2.5
Comparative Example 1	—	—	—	—	—	0.922	0.3	65	—
Comparative Example 2	—	—	—	—	—	0.920	1.0	30	—

	Physical properties of composition					
	Tensile impact strength (kg-cm/cm²)	Olsen's flexural modulus (kg/cm²)	ESCR F_{50} (hr)	Tensile strength (kg/cm²)	Brabender torque (kg · m)	Chlorine water resistance
Example 8	340	2600	1000	290	1.9	1
Comparative Example 1	200	2200	30	180	2.2	5
Comparative Example 2	230	3200	1000	250	2.9	2

*Distribution index of S.C.B. = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)

EXAMPLE 9

The ethylene-α-olefin copolymer A2-1 obtained in Example 4 and the ethylene-α-olefin copolymer B2-1 obtained in Example 5 were mixed at a 50/50 weight ratio and kneaded in a Banbury mixer. A composition having a density, melt index and melt flow ratio shown in Table 8 was prepared. Physical properties of the composition are also shown in Table 8. For the purpose of comparison, in Table 8 are also shown Comparative example 3 using a high pressure method polyethylene based on the conventional technique (commercial product: Sumikathene ®G 701 manufactured by Sumitomo Chemical Co., Ltd.) as well as Comparative example 4 using a low density ethylene-α-olefin copolymer of the conventional technique. As is obvious from Table 8, the polymer composition of this invention has a better fluidity at injection molding than the high pressure polyethylene and, moreover, has a much higher tensile impact strength, rigidity, ESCR and tensile strength. Also, the polymer composition of the present invention is largely excellent in fluidity at injection molding, compared with the low density ethylene-α-olefin copolymer of the conventional technique, and further has a much higher tensile impact strength and ESCR.

EXAMPLES 10 TO 14

Ethylene-α-olefin copolymers A obtained in Example 2 and ethylene-α-olefin copolymers B obtained in Example 3 were mixed in various ratios and the compositions having densities, MIs and MFRs shown in Table 9 are obtained. Their physical properties were also shown in Table 9.

In Table 9 is also shown a similar composition obtained from two stage polymerization (Example 6). For the purpose of comparison, in Table 9 were also shown Comaprative examples 5, 6 and 7 as examples of low density ethylene-α-olefin copolymers of the conventional technique of which molecular weight distributions are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B.

As is obvious from Table 9, in the compositions of this invention, S.C.B. in higher molecular weight components is more than or about equal to that in lower molecular weight components as seen in distribution index of S.C.B. (compare Examples 6, 10 and 14 with Comparative examples 5 and 6, and Example 13 with Comparative example 7). Therefore, the compositions of this invention have much higher tensile impact strengths and tensile strengths than the comparative compositions of the conventional technique do. By comparison of Comparative example 2 in Table 7 with Comparative example 5 in Table 9, it is seen that widening of molecular weight distribution in the manufacture of a low density ethylene-α-olefin copolymer of the conventional technique maintaining density and MI (larger MFR gives wider distribution) results in large reduction in tensile impact strength and tensile strength.

TABLE 8

		Copolymer A		Copolymer B		Properties of composition			
	Mixing method	Designation	% by weight	Designation	% by weight	Density (g/cm³)	MI (g/10 min)	MFR	Distribution index of S.C.B.*
Example 9	Banbury	A2-1	50	B2-1	50	0.924	5	50	2.5
Comparative Example 3	—	—	—	—	—	0.920	6	35	—
Comparative	—	—	—	—	—	0.924	5	30	—

TABLE 8-continued

Example 4	Tensile impact strength (kg-cm/cm²)	Olsen's flexural modulus (kg/cm²)	ESCR F50 (hr)	Tensile strength (kg/cm²)	Spiral blow length (mm)
Example 9	190	2900	100	220	130
Comparative Example 3	120	2100	2	150	120
Comparative Example 4	110	3500	30	180	80

*Distribution index of S.C.B. = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)

TABLE 9

		Copolymer A		Copolymer B		Properties of composition			
	Mixing method	Designation	% by weight	Designation	% by weight	Density (g/cm³)	MI (g/10 min)	MFR	Distribution index of S.C.B.*
Example 6	Two stage polymerization					0.920	0.7	65	(2.3)
Example 10	Solution	A1-2	60	B1-2	40	0.920	0.5	70	1.8
Example 11	Banbury	A1-3	50	B1-3	50	0.920	0.25	80	1.5
Example 12	"	A1-4	50	B1-4	50	0.920	0.8	50	0.7
Example 13	"	A1-11	50	B1-9	50	0.929	1.2	70	3.8
Example 14	Solution	A1-13	60	B1-12	40	0.919	0.5	70	1.7
Comparative Example 5	Banbury	A1-7	50	B1-6	50	0.920	1.1	65	0.37
Comparative Example 6	Solution	A1-8	60	B1-7	40	0.919	0.5	70	0.50
Comparative Example 7	Banbury	A1-12	50	B1-10	50	0.930	1.2	70	0.36

	Physical properties of composition			
	Tensile impact strength (kg-cm/cm²)	Olsen's flexural modulus (kg/cm²)	Tensile strength (kg/cm²)	Tackiness
Example 6	370	2700	300	o
Example 10	480	2600	320	o
Example 11	480	2700	320	o
Example 12	300	2900	260	o
Example 13	250	3700	250	o
Example 14	500	2500	310	o
Comparative Example 5	110	3200	180	x
Comparative Example 6	200	3100	200	x
Comparative Example 7	70	4500	200	o

*Distribution index of S.C.B. = $\frac{\text{(S.C.B. of copolymer A)}}{\text{(S.C.B. of copolymer B)}}$

EXAMPLES 15 TO 17

Ethylene-α-olefin copolymers A obtained in Example 4 and ethylene-α-olefin copolymers B obtained in Example 5 were mixed in various ratios and the compositions having densities, melt indices and melt flow ratios shown in Table 10 were obtained. Their physical properties are also shown in Table 10.

In Table 10 is also shown a similar composition obtained from two stage polymerization (Example 7). For the purpose of comparison, in Table 10 were also shown Comparative examples 8, 9 and 10 as examples of low density ethylene-α-olefin copolymers of the conventional technique of which molecular weight distributions are made wider, and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B.

As is obvious from Table 10, in the compositions of this invention, the higher molecular weight components have larger S.C.B. than the lower molecular weight components do, as seen in distribution index of S.C.B. (compare Examples 7, 15, 16 with Comparative examples 8 and 9, and Example 17 with Comparative example 10). Therefore, the compositions of this invention have much higher tensile impact strengths ESCRs and tensile strengths than the comparative compositions of the conventional technique do. By comparison of Comparative example 4 in Table 8 with Comparative example 9 in Table 10, it is seen that widening of molecular weight distribution in the manufacture of a low density ethylene-α-olefin copolymer of the conventional technique mainteining density and MI (larger MFR gives wider distribution) results in large reduction in tensile impact strength, ESCR and tensile strength.

EXAMPLES 18 TO 20

Ethylene-α-olefin copolymers A obtained in Example 2 and ethylene-α-olefin copolymers B obtained in Example 3 were mixed in various ratios and the compositions having densities, MIs and MFRs shown in Table 11 are obtained. Their physical properties were also shown in Table 11.

For the purpose of comparison, in Table 11 are also shown an example (Comparative example 1) of high pressure polyethylenes of the conventional technique; an example (Comparative example 11) of low density ethylene-α-olefin copolymers of the conventional technique of which molecular weight distributions are made

wider, and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B.; and an example (Comparative example 12, to be compared with Example 19) of ethylene-α-olefin copolymers compositions of which distribution indices of S.C.B. meet the object of this invention but of which lower molecular weight components have a too low intrinsic viscosity.

It is clearly seen from Table 11 that proper selection of distribution index of S.C.B. gives good transparency about equal to that of high pressure polyethylenes as well as a much more excellent tensile impact strength and tensile strength than those of high pressure polyethylenes.

It is learned from comparison of Example 19 with Comparative example 12 that a too low intrinsic viscosity of lower molecular weight components badly affects the tensile impact strength and transparency of the copolymer composition.

TABLE 10

		Copolymer A		Copolymer B		Properties of composition			
	Mixing method	Designation	% by weight	Designation	% by weight	Density (g/cm³)	MI (g/10 min)	MFR	Distribution index of S.C.B.*
Example 7	Two stage polymerization					0.923	6	55	(1.5)
Example 15	Solution	A2-2	50	B2-2	50	0.923	5	50	1.5
Example 16	"	A2-3	30	B2-3	70	0.924	3	60	1.5
Example 17	Banbury	A2-8	45	B2-8	55	0.929	10	45	1.4
Comparative Example 8	Solution	A2-7	50	B2-6	50	0.922	5	50	0.45
Comparative Example 9	Banbury	A2-4	50	B2-5	50	0.920	5	50	0.49
Comparative Example 10	"	A2-9	45	B2-4	55	0.930	10	45	0.40

	Physical properties of composition				
	Tensile impact strength (kg-cm/cm²)	Olsen's flexural modulus (kg/cm²)	ESCR F_{50} (hr)	Tensile strength (kg/cm²)	Tackiness
Example 7	170	3000	50	220	o
Example 15	240	3000	100	250	o
Example 16	190	3000	30	230	o
Example 17	120	4000	5	200	o
Comparative Example 8	100	3600	15	150	x
Comparative Example 9	80	3200	13	130	x
Comparative Example 10	40	4500	1	110	o

*Distribution index of S.C.B. = $\frac{\text{(S.C.B. of copolymer A)}}{\text{(S.C.B. of copolymer B)}}$

TABLE 11

		Copolymer A		Copolymer B		Properties of composition			
	Mixing method	Designation	% by weight	Designation	% by weight	Density (g/cm³)	MI (g/10 min)	MFR	Distribution index of S.C.B.*
Example 18	Solution	A1-5	30	B1-5	70	0.920	0.15	100	1.0
Example 19	"	A1-6	50	B1-11	50	0.920	0.8	50	1.0
Example 20	Banbury	A1-1	50	B1-4	50	0.916	1.1	65	1.6
Comparative Example 1	—	—	—	—	—	0.922	0.3	65	—
Comparative Example 11	Banbury	A1-9	50	B1-6	50	0.920	0.8	50	0.4
Comparative Example 12	"	A1-10	65	B1-8	35	0.920	0.8	50	1.0

	Physical properties of composition					
	Tensile impact strength (kg-cm/cm²)	Olsen's flexural modulus (kg/cm²)	Tensile strength (kg/cm²)	Tackiness	Haze (%)
Example 18	480	2800	320	o	5
Example 19	400	2800	250	o	5
Example 20	420	2100	250	o	5
Comparative Example 1	200	2200	180	o	5
Comparative Example 11	150	3300	200	x	12
Comparative Example 12	130	2800	220	o	15

*Distribution index of S.C.B. = (S.C.B. of co ...mer A)/(S.C.B. of copolymer B)

EXAMPLES 21, 22, 23

Ethylene-α-olefin copolymers A obtained in Example 4 and ethylene-α-olefin copolymers B obtained in Example 5 were mixed at various ratios, and the compo-

sitions having densities, MIs and MFRs shown in Table 12 are obtained. Their physical properties were also shown in Table 12. For the purpose of comparison, in Table 12 are also shown Comparative example 3 using a high pressure polyethylene of the conventional technique; Comparative example 13 using a composition of low density ethylene-α-olefin copolymers of the conventional technique of which molecular weight distribution is made wider and of which lower molecular weight components have more S.C.B. and of which higher molecular weight components have less S.C.B.; and Comparative example 14 (to be compared with Example 22) using a composition of ethylene-α-olefin copolymers of which distribution index of S.C.B. meets the scope of the present invention but of which lower molecular weight components have a too low intrinsic viscosity. It is obvious from Table 12 that proper selection of distribution index of S.C.B. gives good transparency about equal to that of high pressure polyethylenes and much more excellent tensile impact strength, tensile strength and ESCR than those of high pressure polyethylenes. From comparison of Example 22 with Comparative example 14, it is learned that a too low intrinsic viscosity of lower molecular weight components badly affects tensile impact strength and transparency.

TABLE 13

Polymerization method	Polymerization vessel capacity (l)	Catalyst quality (mg)	Co-Catalyst TEA (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (kg/cm²)	C_2' partial pressure (kg/cm²)	Polymerization temperature (°C.)	Polymerization time (min)
Slurry	65	197	100	C_4 7.0	C_4' 7.16	4.2	10	50	100

Note:
TEA = Triethyl aluminum
C_2' = Ethylene
C_4 = n-Butene
C_4' = Butene-1

TABLE 12

	Mixing method	Copolymer A Designation	Copolymer A % by weight	Copolymer B Designation	Copolymer B % by weight	Properties of composition: Density (g/cm³)	MI (g/10 min)	MFR	Distribution index of S.C.B.*
Example 21	Solution	A2-10	50	B2-9	50	0.923	5	50	0.72
Example 22	Banbury	A2-5	50	B2-4	50	0.922	5	50	1.0
Example 23	"	A2-1	50	B2-4	50	0.920	5	50	1.6
Comparative Example 13	"	A2-6	50	B2-5	50	0.923	5	50	0.37
Comparative Example 14	"	A2-8	65	B2-7	35	0.922	5	50	1.2
Comparative Example 3	—	—	—	—	—	0.920	6	35	—

	Physical properties of composition: Tensile impact strength (kg-cm/cm²)	Olsen's flexural modulus (kg/cm²)	ESCR F_{50} (kg/cm²)	Tensile strength at break	Tackiness (%)	Haze
Example 21	200	3100	20	250	o	7
Example 22	170	2900	30	220	o	7
Example 23	260	2500	200	230	o	7
Comparative Example 13	50	3600	10	130	x	12
Comparative Example 14	80	3200	30	190	o	12
Comparative Example 3	120	2100	2	150	o	7

*Distribution index of S.C.B. = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)

COMPARATIVE EXAMPLE 1

A commercial high pressure polyethylene (Sumikathene ®F101-1 manufactured by Sumitomo Chemical Co., Ltd.) was measured for its physical properties and subjected to blow molding.

Results are shown in Table 7 and 11.

COMPARATIVE EXAMPLE 2

An ethylene-α-olefin copolymer of the conventional technique was synthesized employing polymerization conditions as shown in Table 13 in which the catalyst prepared in Example 1 and triethyl aluminum (co-catalyst) were used. The copolymer gave: density 0.920 g/cm³, MI 1.0 g/10 min., MFR 30. Its physical properties are shown in Table 7.

COMPARATIVE EXAMPLE 3

A commercial high pressure polyethylene (Sumikathene ®G701 manufactured by Sumitomo Chemical Co., Ltd.) was measured for its physical properties and subjected to injection molding.

Results are shown in Table 8 and 12.

COMPARATIVE EXAMPLE 4

A low density ethylene-α-olefin copolymer of the conventional technique was synthesized employing polymerization conditions shown in Table 14 in which the catalyst prepared in Example 1 and triethyl aluminum (co-catalyst) were used. The copolymer gave: density 0.924 g/cm³, melt index 5 g/10 min., melt flow ratio 30. Its physical properties are shown in Table 8.

TABLE 14

Polymerization method	Polymerization vessel capacity (l)	Catalyst quality (mg)	Co-Catalyst TEA (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (kg/cm^2)	C_2' partial pressure (kg/cm^2)	Polymerization temperature (°C.)	Polymerization time (min)
Slurry	65	199	25	C_4 6.0	C_4' 6.14	10.2	11.3	50	90

Note:
TEA = Triethyl aluminum
C_2' = Ethylene
C_4 = n-Butane
C_4' = Butene-1

COMPARATIVE EXAMPLES 5, 6, 7 AND 11

Compositions of ethylene-α-olefin copolymers of the conventional technique were prepared by blending ethylene-α-olefin copolymers A obtained in Example 2 and ethylene-α-olefin copolymers B obtained in Example 3 at ratios shown in Table 9 or 11. However in these copolymer compositions, molecular weight distributions are made wider and lower molecular weight components have larger S.C.B. and higher molecular weight components have smaller S.C.B. Densities, MIs, MFRs and physical properties of these compositions are shown in Table 9 or 11.

COMPARATIVE EXAMPLE 12

By blending an ethylene-α-olefin copolymer A obtained in Example 2 and an ethylene-α-olefin copolymer B obtained in Example 3 at a mixing ratio shown in Table 11, a composition of ethylene-α-olefin copolymers was prepared of which distribution index of S.C.B. meets the scope of the present invention but of which lower molecular weight components have a too low intrinsic viscosity. Its density, MI, MFR and physical properties are shown in Table 11.

COMPARATIVE EXAMPLES 8, 9, 10 AND 13

Compositions of ethylene-α-olefin copolymers of the conventional technique were prepared by blending ethylene-α-olefin copolymers A obtained in Example 4 and ethylene-α-olefin copolymers B obtained in Example 5 at mixing ratios shown in Table 10 or 12. However in these compositions, molecular weight distributions are made wider and lower molecular weight components have larger S.C.B. and higher molecular weight components have smaller S.C.B. Densities, MIs, MFRs and physical properties of these compositions are shown in Table 10 or 12.

COMPARATIVE EXAMPLE 14

By blending an ethylene-α-olefin copolymer A obtained in Example 4 and an ethylene-α-olefin copolymer B obtained in Example 5 at a mixing ratio shown in Table 12, a composition of ethylene-α-olefin copolymers was prepared of which distribution index of S.C.B. meets the scope of this invention but of which lower molecular weight components have too low an intrinsic viscosity. Its density, MI, MFR and physical properties are shown in Table 12.

EXAMPLE 24

Ethylene-α-olefin copolymers A were polymerized using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing α-olefins and other polymerization conditions as shown in Table 15. Their densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) are shown in Table 15.

These polymers are used in the following examples as mixing components.

TABLE 15

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)
A3-1	Slurry	65	131	TEA 100	C_4 6.0	C_4' 6.14
A3-2	Solution	1	25.1	DEAC 2.5	C_7 0.22	4-MP-1 0.130
A3-3	"	1	24.8	"	C_7 0.30	C_4' 0.055
A3-4	Slurry	65	307	TEA 100	C_4 6.0	C_4' 6.14
A3-5	"	65	130	TEA 50	"	"
A3-6	"	65	125	"	"	"
A3-7	"	65	301	TEA 100	"	"
A3-8	"	65	318	"	"	"
A3-9	"	65	308	"	"	"

No.	H_2 partial pressure (kg/cm^2)	C_2' - partial pressure (kg/cm^2)	Polymerization temperature (°C.)	Properties: Density (g/cm^3)	[η] (dl/g)	S.C.B.	$\overline{Mw}/\overline{Mn}$
A3-1	0.45	5.0	50	0.899	2.6	38	5.9
A3-2	0.10	20	140	0.899	2.6	27	3.5
A3-3	0.10	20	140	0.902	2.6	24	3.7
A3-4	0.9	9.0	50	0.914	2.4	22	6.0
A3-5	0.22	5.5	50	0.906	3.2	28	5.8
A3-6	1.8	18	50	0.923	2.6	9	5.5
A3-7	1.2	12	50	0.919	2.4	16	5.8
A3-8	2.0	20	50	0.928	2.4	8	5.4

TABLE 15-continued

A3-9	1.4	9.0	50	0.914	2.2	22	5.7

Note
TEA = triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1 = 4-Methylpentene
C_2' = Ethylene
C_4 = n-Butane
C_4' = Butene-1
C_6' = Hexene-1
C_7 = n-Heptane

EXAMPLE 25

Ethylene-α-olefin copolymers B were polymerized using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing α-olefins and other polymerization conditions shown in Table 16. Their densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) are shown in Table 16.

These copolymers are used in the following examples as mixing components.

TABLE 16

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)
B3-1	Slurry	65	405	TEA 50	C_6 12.0	C_6' 2.0
B3-2	Solution	1	25.5	DEAC 2.5	C_7 0.30	4-MP-1 0.025
B3-3	"	1	24.2	DEAC 2.5	C_7 0.32	C_6' 0.013
B3-4	Slurry	65	330	TEA 100	C_4 15.2	C_6' 0.7
B3-5	"	65	391	TEA 100	"	C_6' 1.8
B3-6	"	65	408	TEA 100	C_4 12.0	C_6' 4.0
B3-7	"	65	350	TEA 100	C_4 15.2	C_6' 1.3
B3-8	"	65	405	TEA 50	"	C_6' 1.6
B3-9	"	65	390	TEA 100	"	C_6' 0.20

No.	H_2 partial pressure (kg/cm^2)	C_2'-partial pressure (kg/cm^2)	Polymerization temperature (°C.)	Properties: Density (g/cm^3)	[η] (dl/g)	S.C.B.	$\overline{Mw}/\overline{Mn}$
B3-1	10.8	8.3	70	0.942	0.83	15	5.5
B3-2	2.4	10	140	0.943	0.81	10	3.7
B3-3	2.4	10	140	0.940	0.82	13	3.8
B3-4	7.5	5.0	70	0.949	0.75	11	5.3
B3-5	7.2	8.0	70	0.941	0.92	14	5.4
B3-6	5.2	4.0	50	0.910	0.82	35	5.9
B3-7	7.5	5.0	70	0.942	0.75	16	5.8
B3-8	8.8	5.0	70	0.935	0.24	20	5.9
B3-9	15.0	1.5	70	0.949	0.27	11	5.6

Note
TEA = triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1 = 4-Methylpentene
C_2' = Ethylene
C_4 = n-Butane
C_4' = Butene-1
C_6' = Hexene-1
C_7 = n-Heptane

EXAMPLE 26

A composition of ethylene-α-olefin copolymers was prepared from a two stage polymerization. The first stage polymerization was carried out for 90 min, using the catalyst obtained in Example 1 and triethyl aluminum (co-catalyst) and employing other polymerization conditions shown in Table 17.

Successively the second stage polymerization was conducted for 150 min. by changing only the hydrogen partial pressure and the ethylene partial pressure as shown in table 17. In both stages, the liquid phase molar ratio of ethylene, butene-1 and hydrogen were kept at respective fixed levels. Polymerized quantities in each stage were calculated from quantities of fed ethylene. The total polymer consisted of about 50% by weight of lower molecular weight components. Immediately before the completion of the first stage polymerization, a part of the polymer formed was taken out as a polymer sample of the first stage and measured for its density, intrinsic viscosity, S.C.B. and (weight average molecular weight/number average molecular weight). Similar measurements were also made for the whole polymer of this two stage polymerization. From the values of the first stage polymer and the whole polymer, the intrinsic viscosity and S.C.B. of the polymer formed in the second stage along were calculated, and they are shown in Table 17. The whole polymer gave: density 0.919 g/cm^3, melt index 0.5 g/10 min., melt flow ratio 70, intrinsic viscosity 1.70 dl/g, S.C.B. 27. The flow characteristics and the solid physical properties of the whole polymer are shown in Table 19.

EXAMPLE 27

By mixing the ethylene-α-olefin copolymer A3-1 obtained in Example 24 and the ethylene-α-olefin copolymer B3-1 obtained in Example 25 at a 50/50 weight

ratio and kneading the mixture in a Banbury mixer, a composition having the density, MI and MFR as shown in Table 18 was prepared. The physical properties of this composition are also shown in Table 18.

For the purpose of comparison, in Table 18 are also shown Comparative examples 15 and 16 using high pressure polyethylenes of the conventional technique (commercial products Sumikathene ®F208-1, F101-1 manufactured by Sumitomo Chemical Co., Ltd.) as well as Comparative example 17 using a low density ethylene-α-olefin copolymer of the conventional technique.

It is obvious from Table 18 that the copolymer composition of this invention has a Brabender torque about equal to those of high pressure polyethylenes (good in processability) and is quite excellent in tensile impact strength, rigidity, ESCR and tensile strength, compared with these polyethylenes.

When compared with the low density ethylene-α-olefin copolymer of the conventional technique, this composition has a much smaller Brabender torque (processability is much better), a superior tensile impact strength and tensile strength.

TABLE 17

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)
1st stage	Slurry	5	24.3	5	C_4 1000	C_4 250
2nd stage	Slurry					

No.	H_2 partial pressure (kg/cm^2)	C_2' - partial pressure (kg/cm^2)	Polymerization temperature (°C.)	Polymerization time (min)	Properties: Density (g/cm^3)	[η] (dl/g)	S.C.B.	$\overline{Mw}/\overline{Mn}$
1st stage	0.4	3	50	90	0.900	2.6	37	5.8
2nd stage	14	8		150	—	(0.8)	(17)	—

Note
C_4 = n-Butane
TEA = Triethyl aluminum
C_4' = Butene-1
( ) = Calculated values
C_2' = Ethylene

TABLE 18

	Mixing method	Copolymer A: Designation	Copolymer A: % by weight	Copolymer B: Designation	Copolymer B: % by weight	Properties of composition: Density (g/cm^3)	MI (g/10 min)	MFR	Distribution index of S.C.B.*
Example 27	Banbury	A3-1	50	B3-1	50	0.920	0.5	70	2.5
Comparative Example 15	—	—	—	—	—	0.923	1.4	50	—
Comparative Example 16	—	—	—	—	—	0.922	0.3	65	—
Comparative Example 17	—	—	—	—	—	0.920	0.5	30	—

	Physical properties of composition: Tensile impact strength (kg-cm/cm^2)	Olsen's flexural modulus (kg/cm^2)	ESCR F_{50} (hr)	Tensile strength (kg/cm^2)	Brabender torque (kg · m)
Example 27	450	2600	>1000	320	2.0
Comparative Example 15	130	2400	0.3	160	1.9
Comparative Example 16	200	2200	30	180	2.2
Comparative Example 17	280	3200	>1000	260	3.5

*Distribution index of S.C.B. = $\frac{\text{(S.C.B. of copolymer A)}}{\text{(S.C.B. of copolymer B)}}$

EXAMPLES 28 TO 31

Compositions having densities, MIs and MFRs shown in Table 19 were obtained, by blending ethylene-α-olefin copolymers A obtained in Example 24 and ethylene-α-olefin copolymers B obtained in Example 25 at mixing ratios as shown in Table 19. The physical properties of these compositions are shown in Table 19.

In Table 19 are also shown a composition of similar ethylene-α-olefin copolymers synthesized in two stage polymerization (Example 26) as well as, for comparison, ethylene-α-olefin copolymers compositions (Comparative examples 18, 19, 20) of which higher molecular weight components have smaller S.C.B. than lower molecular weight components do or have relatively few S.C.B. Also as shown in Table 19 an ethylene-α-olefin copolymers composition (Comparative example 21, to be compared with Examples 30 and 31) of which distri-

bution index of S.C.B. meets the scope of the presetn invention but of which lower molecular weight components have too low an intrinsic viscosity.

As is obvious from Table 19, in the compositions of this invention, higher molecular weight components have larger S.C.B. than lower molecular weight components do. (Comparison should be made between Examples 26, 28 and 29 and Comparative example 18, and also between Example 30 and 31 and Comparative examples 19 and 20.) The compositions of this invention are also far superior in tensile impact strength and tensile strength to the Comparative examples.

is far superior to those of the high pressure polyethylenes, in dart impact strength, Elmendorf tear strengths (absolute value and MD/TD balance), tensile strength, heat-sealing characteristics, hot tack property and heat sealing strength in contaminated condition.

In the film of the composition prepared in Example 27, heat-sealing strength and heat sealing strength in contaminated condition had about same values, while, in the films of Comparative examples 15 and 16, heat sealing strength in contaminated condition were slightly lower than heat-sealing strength.

The measurement methods of the physical properties

TABLE 19

		Properties of composition											
		Copolymer A		Copolymer B		Density	MI (g/10 min.)	MFR	Distribution index of S.C.B.*	Tensile impact strength (kg-cm/cm²)	Olsen's flexural modulus (kg/cm²)	Tensile strength (kg/cm²)	Tackiness
	Mixing method	Designation	% by weight	Designation	% by weight	(g/cm³)							
Example 26	—	—	—	—	—	0.919	0.5	70	(2.2)	470	2500	320	o
Example 28	Solution	A3-2	50	B3-2	50	0.920	0.5	70	2.7	350	2600	340	o
Example 29	"	A3-3	50	B3-3	50	0.920	0.5	70	2.0	320	2600	320	o
Example 30	Banbury	A3-4	50	B3-4	50	0.929	0.8	50	2.0	300	4000	300	o
Example 31	Solution	A3-5	30	B3-5	70	0.929	0.8	50	2.0	280	4000	290	o
Comparative Example 18	Banbury	A3-6	50	B3-6	50	0.920	0.5	70	0.26	150	3300	210	x
Comparative Example 19	"	A3-7	50	B3-7	50	0.929	0.8	50	1.0	200	4200	240	o
Comparative Example 20	"	A3-8	50	B3-8	50	0.929	0.8	50	0.4	90	4500	200	o
Comparative Example 21	"	A3-9	65	B3-9	35	0.929	0.8	50	2.0	120	4000	230	o

*Distribution index of S.C.B. = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)

EXAMPLE 32

The composition prepared in Example 27 and the low density ethylene-α-olefin copolymer of the conventional technique used in Comparative example 17 were subjected to film processing under the following conditions.

Processing conditions

Extruder: Tanabe 30 mmϕ extruder

Screw: Full flight L/D=28, C.R.=2.5

Die: Diameter 50 mm, die gap 2.0 mm

Temperature control: C_1 170°, C_2 220°, C_3 220°, HD 220° C.

Screw revolution: 35 rpm

Output: 3.2 kg/hr

Blow up ratio: 2.5

Frost line height: 180 mm

Take-off speed: 5 m/min

Film thickness: 35μ

Also, the commercial high pressure polyethylenes used in Comparative examples 15 and 16 were subjected to film processing under the following conditions.

Die gap: 1.0 mm

Temperature control: C_1 140°, C_2 160°, C_3 160°, HD 160° C.

(Other conditions were same as those applied above.)

In the case of the low density ethylene-α-olefin copolymer of the conventional technique used in Comparative example 17, a satisfactory film was not obtained with too much load put on the motor and with shark skin formed on the film surface.

In the cases of the composition prepared in Example 27 and the commercial high pressure polyethylenes used in Comparative examples 15 and 16, satisfactory films were obtained with no excessive motor loads. The physical properties of these films were shown in Table 20. The film of the composition prepared in Example 27 shown in table 20 are described below.

Dart impact strength: In accordance with ASTM D 1709A.

Elmendorf tear strength: In accordance with JIS Z 1702.

Tensile strength: In accordance with JIS K 6732-62

Heat-sealing characteristics: Heat-sealing strength of a film heat-sealed with a heat sealer of bar type. The maximum heat-sealing strength was obtained when pulled under conditions of film thickness of 35μ, width of 15 mm and pulling speed of 200 mm/min. after heat-sealing under sealing pressure of 1 kg/cm², 0.5 sec. and each incremental 5° C.

Hot tack property: A test sample (25 mm wide and 400 mm long) was folded into two, and the one end was fixed to the upper clamp and a stripping weight was placed on the other end. The area near the crease was inserted between heating bars and heat-sealed under a sealing pressure of 1 kg/cm² for 0.5 sec., and then the length of the stripped surface was measured.

Heat Sealing strength in contaminated condition: This is a test method for evaluating the heat-sealing characteristics in the condition that the heat-sealed surface is soiled with contents such as mayonaise, edible oils and flours. Specifically, a test film sample was folded in such a way that the surface soiled with an edible oil came inside, and was heat-sealed under the same conditions as used in heat-sealing characteristics. Then, its heat-sealing strength was measured.

COMPARATIVE EXAMPLE 15

A commercial high pressure poiyethylene (Sumikathene ®F208-1 manufactured by Sumitomo Chemical Co., Ltd.) was subjected to measurement of physical

properties and film processing. Results are shown in Tables 18 and 20.

COMPARATIVE EXAMPLE 16

A commercial high pressure polyethylene (Sumikathene ®F 101-1 manufactured by Sumitomo Chemical Co., Ltd.) was subjected to measurements of physical properties and film processing. Results are shown in Tables 18 and 20.

COMPARATIVE EXAMPLE 17

A low density ethylene-α-olefin copolymer of the conventional technique was synthesized, using the catalyst produced in Example 1 and triethyl aluminum (co-catalyst) and employing the other copolymerization conditions shown in Table 21. The copolymer gave: density 0.920 g/cm³, MI 0.5 g/10 min., MFR 30. The physical properties of this polymer are shown in Table 18.

COMPARATIVE EXAMPLES 18, 19, 20

Compositions of ethylene-α-olefin copolymers of the conventional technique were prepared, by mixing ethylene-α-olefin copolymers A obtained in Example 24 and ethylene-α-olefin copolymers B obtained in Example 25 at ratios shown in Table 19. In these compositions, molecular weight distributions are made wider and lower molecular weight components have larger S.C.B. and higher molecular weight components have smaller S.C.B. Densities, MIs, MFRs and physical properties of these compositions are shown in Table 19.

COMPARATIVE EXAMPLE 21

By mixing an ethylene-α-olefin copolymer A obtained in Example 24 and an ethylene-α-olefin copolymer B obtained in Example 25 at a ratio as shown in Table 19, a composition of ethylene-α-olefin copolymers were prepared of which distribution index of S.C.B., meets the scope of this invention but of which lower molecular weight weight components have a too low intrinsic viscosity. Its density, MI, MFR and physical properties were shown in Table 19.

TABLE 20

	Dart impact strength (kg · cm/mm)	Elmendorf tear strength MD/TD (kg/cm)	Tensile strength MD/TD (kg/cm²)	Heat-sealing strength (kg/15mm width)	Hot tack property (mm)	Heat sealing strength in contaminated condition
Example 27	700	120/150	450/410	1.5	1.0	o
Comparative Example 15	270	80/50	250/210	0.7	4.0	Δ
Comparative Example 16	250	70/70	280/250	0.7	3.0	Δ

TABLE 21

Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst TEA (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (kg/cm²)	C'_2 partial pressure (kg/cm²)	Polymerization temperature (°C.)	Polymerization time (min)
Slurry	65	202	100	C_4 7.0	C'_4 7.16	3.0	10	50	90

Note
TEA = Triethyl aluminum
C_4 = n-Butene
C'_4 = Butene-1
C'_2 = Ethylene

EXAMPLE 33

Ethylene-α-olefin copolymers A were synthesized using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing α-olefins and other polymerization conditions as shown in Table 22. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these copolymers are shown in Table 22.

These copolymers are used in the following examples as mixing components.

EXAMPLE 34

Ethylene-α-olefin copolymers B were synthesized using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing α-olefins and other polymerization conditions as shown in Table 23. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these copolymers are shown in Table 23.

These copolymers are used in the following examples as mixing components.

TABLE 22

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (mg)	α-olefin (kg)	H_2 partial pressure (kg/cm²)	C'_2 partial pressure (kg/cm²)	Polymerization temperature (°C.)	Properties: Density (g/cm³)	Properties: [η] (dl/g)	Properties: S.C.B.	Properties: Mw/Mn
A4-1	Slurry	65	310	TEA	C_4 6.0	C'_4 6.14	0.70	7.8	50	0.912	2.6	24	5.6

TABLE 22-continued

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (mg)	α-olefin (kg)	H_2 partial pressure (kg/cm²)	C'_2 partial pressure (kg/cm²)	Polymerization temperature (°C.)	Properties: Density (g/cm³)	[η] (dl/g)	S.C.B.	Mw/Mn
A4-2	Solution	1	24.3	DEAC 100 2.5	C_7 0.27	4-MP-1 0.090	0.15	20	140	0.912	2.5	17	3.4
A4-3	Slurry	65	83	TEA 50	C_4 6.0	C'_4 6.14	0.09	7.0	50	0.912	4.4	20	5.8
A4-4	"	65	309	TEA 100	"	"	1.2	3.0	50	0.911	2.2	25	5.7
A4-5	"	65	145	TEA 50	"	"	0.59	6.7	50	0.906	2.6	29	5.8
A4-6	Solution	1	25.2	DEAC 2.5	C_7 0.30	C'_6 0.035	0.2	20	140	0.909	2.2	18	3.4
A4-7	Slurry	65	303	TEA 100	C_4 6.0	C'_4 6.14	0.36	9.0	50	0.917	3.3	16	5.6
A4-8	"	65	125	TEA 100	"	"	1.8	18	50	0.923	2.6	9	5.5
A4-9	Solution	1	24.5	DEAC 2.5	C_7 0.40	4-MP-1 0.040	0.25	20	140	0.923	2.5	8	3.3
A4-10	Slurry	65	121	TEA 100	C_4 6.0	C'_4 3.7	1.2	20	50	0.925	3.3	6	5.5
A4-11	"	65	302	TEA 100	"	C'_6 6.14	1.4	8.5	50	0.913	2.1	23	5.4

Note
TEA = Triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1 = 4-Methylpentene-1
C_4 = n-Butane
C'_4 = Butene-1
C'_6 = Hexene-1
C_7 = n-Heptane

TABLE 23

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (mg)	α-olefin (kg)	H_2 partial pressure (kg/cm²)	C'_2 partial pressure (kg/cm²)	Polymerization temperature (°C.)	Properties: Density (g/cm³)	[η] (dl/g)	S.C.B.	Mw/Mn
B4-1	Slurry	65	402	TEA 50	C_4 12.0	C'_4 3.2	7.8	6	70	0.929	0.85	24	5.8
B4-2	Solution	1	24.2	DEAC 2.5	C_7 0.80	4-MP-1 0.045	2.2	10	140	0.929	0.81	17	3.6
B4-3	Slurry	65	405	TEA 50	C_4 12.0	C'_4 3.2	7.0	6	70	0.928	0.90	24	5.7
B4-4	"	65	425	TEA 50	C_4 13.2	C'_4 2.0	10.5	5	70	0.929	0.65	25	5.7
B4-5	"	65	411	TEA 50	"	C'_4 1.6	6.5	5	70	0.935	0.83	20	5.5
B4-6	Solution	1	25.1	DEAC 2.5	C_7 0.82	C'_6 0.017	2.7	10	140	0.926	0.63	18	3.5
B4-7	Slurry	65	346	TEA 100	C_4 15.2	C'_4 1.1	12	3	70	0.941	0.52	16	5.4
B4-8	"	65	408	TEA 100	C_4 12.0	C'_4 4.0	5.2	4	50	0.910	0.82	35	5.9
B4-9	Solution	1	24.9	DEAC 2.5	C_7 0.28	4-MP-1 0.055	2.0	10	140	0.912	0.85	22	3.7
B4-10	Slurry	65	250	TEA 100	C_4 15.2	C'_4 0.4	13.5	1.5	50	0.930	0.28	25	5.7
B4-11	"	65	410	TEA 50	"	C'_4 1.4	12	3	70	0.934	0.53	22	5.8
B4-12	"	65	290	TEA 50	C_4 6.0	C'_4 6.14	8.1	9	50	0.927	1.2	23	5.7

Note
TEA = Triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1 = 4-Methylpentene-1
C_4 = n-Butane
C'_4 = Butene-1
C'_6 = Hexene-1
C_7 = n-Heptane

EXAMPLE 35

A composition of ethylene-α-olefin copolymers was prepared in two stage polymerization. The first stage polymerization was carried out for 70 min. using the catalyst produced in Example 1 and triethyl alminum (co-catalyst) and other polymerization conditions as

shown in Table 24. Successively, the second stage polymerization was conducted for 180 min. by changing only the hydrogen partial pressure and the ethylene partial pressure as shown in Table 24. In both stages, the liquid phase molar ratio of ethylene, butene-1 and hydrogen was kept at respective fixed levels. The polymerized quantities in each stage were calculated from the quantities of fed ethylene. The copolymers consisted of about 50% by weight of higher molecular weight components and about 50% by weight of lower molecular weight components. Immediately before the completion of the first stage polymerization, a part of the polymer was taken out and measured for its density, intrinsic viscosity, S.C.B. and (weight average molecular weight/number average molecular weight). The whole polymer obtained after the second stage was also measured for the same test items. From the values of the first stage polymer and the whole polymer, the intrinsic viscosity and S.C.B. of the polymer formed in the second stage alone were calculated. These values were shown in Table 24. The whole polymer gave: density 0.921 g/cm^3, MI 0.5 g/10 min., MFR 70, intrinsic viscosity 1.7 dl/g, S.C.B. 24. Flow characteristics and solid physical properties of the whole polymer were shown in Table 26.

EXAMPLE 36

By mixing the ethylene-α-olefin copolymer A4-1 obtained in Example 33 and the ethylene-α-olefin copolymer B4-1 obtained in Example 34 at a 50/50 weight ratio and kneading the mixture in a Banbury mixer, a composition of ethylene-α-olefin copolymers having the density, MI and MFR shown in Table 25 was prepared. Physical properties of this composition were also shown in Table 25. For comparison, in Table 25 were also shown Comparative examples 15 and 16 using high pressure polyethylenes of the conventional technique (commercial product Sumikathene ®F 208-1, F 101-1 manufactured by Sumitomo Chemical Co., Ltd.) as well as Comparative example 17 using a low density ethylene-α-olefin copolymer of the conventional technique.

As is obvious from Table 25, the polymer composition of the present invention, when compared with high pressure polyethylenes, has about an equal Brabender torque (satisfactory in processability), and is much superior in tensile impact strength, rigidity, ESCR and tensile strength, and further is about equally satisfactory in transparency.

Compared with the low density ethylene-α-olefin copolymer of the conventional technique, this polymer composition has a much lower Brabender torque (far more excellent in processability) and a higher tensile impact strength and tensile strength.

EXAMPLES 38, 39, 40, 41, 42, 43

By mixing the ethylene-α-olefin copolymers A obtained in Example 33 and the ethylene-α-olefin copolymers B obtained in Example 34 at ratios as shown in Table 26, compositions having densities, MIs and MFRs shown in Table 26 were obtained. Physical properties of these compositions are also shown in Table 26.

In Table 26 are also shown a similar composition prepared by two stage polymerization (Example 35) and, for the purpose of comparison, compositions of low density ethylene-α-olefin copolymers of the conventional technique (Comparative examples 22, 23, 25) of which molecular weight distributions are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B. In Table 26 is also shown a composition of ethylene-α-olefin copolymers (Comparative examples 24, to be compared with Examples 40 and 42) of which distribution index of S.C.B. meets the scope of this invention but of which lower molecular weight components have a too low intrinsic viscosity.

As seen in Table 26, in the compositions of this invention, S.C.B. of higher molecular weight components are more than or about equal to those of lower molecular weight components. (Compare Examples 35, 38 and 41 with Comparative examples 22 and 23, and Example 43 with Comparative example 25.) Therefore, compared with the compositions of the conventional technique, the compositions of this invention are far excellent in tensile impact strength and tensile strength, and are superior in transparency.

From the comparison between Comparative example 17 of Table 25 and Comparative example 22 of Table 26, it is learned that widening of molecular weight distribution (higher MFR gives wider distribution) in the manufacture of a low density ethylene-α-olefin copolymer of the conventional technique with its density and MI kept constant results in large reduction in tensile impact strength and tensile strength.

From the comparison of Examples 40 and 42 with Comparative example 24, it is learned that a too low intrinsic viscosity of lower molecular weight components badly affects its tensile impact strength, tensile strength and transparency.

TABLE 24

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst TEA (mmol)	Solvent (g)	α-olefin (g)	H_2 partial pressure (kg/cm^2)	C_2-partial pressure (kg/cm^2)	Polymerization temperature (°C.)	Polymerization time (min)	Properties: Density (g/cm^3)	Properties: [η] (dl/g)	Properties: S.C.B.	Properties: $\overline{Mw}/\overline{Mn}$
1st stage	Slurry	5	24.3	5	C_4 1000	C'_4 250	0.6	4	50	70	0.912	2.6	24	5.7
2nd stage	Slurry						10	5		180	—	(0.8)	(23)	—

Note
C_4 = n-Butane
C'_4 = Butene-1
C_2 = Ethylene
TEA = Triethyl aluminum
( ) = Calculated value

TABLE 25

	Mixing method	Copolymer A Designation	Copolymer A % by weight	Copolymer B Designation	Copolymer B % by weight	Properties of composition: Density (g/cm³)	MI (g/10 min.)	MFR	Distribution index of S.C.B.*
Example 36	Banbury	A4-1	50	B4-1	50	0.920	0.5	70	1.0
Example 37	"	A4-11	50	B4-12	50	0.921	0.7	40	1.0
Comparative Example 15	High pressure polyethylene (Sumikathene ® F208-1)					0.923	1.4	50	—
Comparative Example 16	High pressure polyethylene (Sumikathene ® F101-1)					0.922	0.3	65	—
Comparative Example 17	Low density ethylene/α-olefin copolymer of the conventional technique					0.920	0.5	30	—

	Physical properties of composition: Tensile impact strength (kg-cm/cm²)	Olsen's flexural modulus (kg/cm²)	ESCR F_{50} (hr)	Tensile strength (kg/cm²)	Haze (%)	Brabender torque (kg · m)
Example 36	350	2800	>1000	280	5	2.0
Example 37	370	3000	>1000	290	5	2.6
Comparative Example 15	130	2400	0.3	160	4	1.9
Comparative Example 16	200	2200	30	180	6	2.2
Comparative Example 17	280	3200	>1000	260	5	3.5

*Distribution index of S.C.B. = $\frac{\text{(S.C.B. of copolymer A)}}{\text{(S.C.B of copolymer B)}}$

TABLE 26

	Mixing method	Copolymer A Designation	Copolymer A % by weight	Copolymer B Designation	Copolymer B % by weight	Properties of composition: Density (g/cm³)	MI (g/10 min.)	MFR	Distribution index of S.C.B.*	Physical properties of composition: Tensile impact strength (kg-cm/cm²)	Olsen's flexural modulus (kg/cm²)	Tensile strength (kg/cm²)	Haze (%)	Tackiness
Example 35	Two stage polymerization					0.921	0.5	70	(1.0)	340	2800	280	6	o
Example 38	Solution	A4-2	50	B4-2	50	0.920	0.6	70	1.0	430	2800	320	5	o
Example 39	"	A4-3	30	B4-3	70	0.921	0.3	90	0.8	370	2800	300	7	o
Example 40	Banbury	A4-4	50	B4-4	50	0.920	1.1	65	1.0	290	2800	250	6	o
Example 41	"	A4-5	50	B4-5	50	0.920	0.5	70	1.5	400	2700	300	8	o
Example 42	Solution	A4-6	50	B4-6	50	0.920	1.1	65	1.0	360	2800	310	5	o
Example 43	Banbury	A4-7	50	B4-7	50	0.929	0.2	10	1.0	370	4200	300	8	o
Comparative Example 22	"	A4-8	50	B4-8	50	0.920	0.5	70	0.26	150	3300	210	12	X
Comparative Example 23	Solution	A4-9	50	B4-9	50	0.920	0.6	65	0.36	180	3200	220	12	Δ
Comparative Example 24	Banbury	A4-4	65	B4-10	35	0.920	0.8	50	1.0	130	2800	220	15	o
Comparative Example 25	"	A4-10	50	B4-11	50	0.930	0.2	100	0.27	170	4800	230	20	o

*Distribution index of S.C.B. = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)

EXAMPLE 44

The compositions prepared in Examples 36 and 37 as well as the low density ethylene-α-olefin copolymer of the conventional technique used in Comparative example 17 were subjected to film processing in the same conditions as used in Example 32.

The commercial high pressure polyethylenes used in Comparative examples 15 and 16 were also subjected to film processing in the same conditions. A satisfactory film was not obtained from the low density ethylene-α-olefin copolymer of the conventional technique used in Comparative example 17, with too much load put on the motor and with shark skin formed on the film surface.

Satisfactory films having good transparency were obtained from the compositions prepared in Examples

36 and 37 and the commercial high pressure polyethylenes used in Comparative examples 15 and 16, with no problem of motor load. Physical properties of these films are shown in Table 27. Compared with the films of the high pressure method polyethylenes, the films of the compositions prepared in Examples 36 and 37 had about same transparency but were superior in dart impact strength, Elmendorf tear strength (absolute value property and MD/TD balance), heat-sealing properties, tensile strength, hot tack and heat sealing strength in contaminated condition. In case of the films of the compositions prepared in Examples 36 and 37, heat-sealing strengths and heat sealing strength in contaminated condition were at about same levels, but in the films of the high pressure polyethylenes of Comparative example 16, heat sealing strength in contaminated condition were lower than heat-sealing strengths.

COMPARATIVE EXAMPLES 22, 23, 25

By mixing ethylene-α-olefin copolymers A obtained in Example 33 and ethylene-α-olefin copolymers B obtained in Example 34 at ratios as shown in Table 26, compositions of low density ethylene-α-olefin copolymers of the conventional technique were prepared of which molecular weight distribution are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B. Densities, MIs, MFRs and physical properties of these compositions are shown in Table 26.

COMPARATIVE EXAMPLE 24

By mixing an ethylene-α-olefin copolymer A obtained in Example 33 and an ethylene-α-olefin copolymer B obtained in Example 34 at a ratio shown in Table 26, a composition of ethylene-α-olefin copolymers was prepared of which distribution index of S.C.B. meets the scope of this invention but of which lower molecular weight components have a too low intrinsic viscosity. Its density, MI, MFR and physical properties are shown in Table 26.

TABLE 27

	Haze (%)	Dart impact strength (kg · cm/mm)	Elmendorf tear strength MD/TD (kg/cm)	Tensile strength MD/TD (kg/cm²)	Heat-sealing strength (kg/15 mm width)	Hot tack property (mm)	Heat sealing strength in contaminated condition
Example 36	5	500	90/120	410/380	1.2	2.0	o
Example 37	5	450	60/120	420/370	1.3	2.0	o
Comparative Example 15	4	270	20/50	250/210	0.7	4.0	Δ
Comparative Example 16	7	250	70/70	280/250	0.7	3.0	Δ

EXAMPLE 45

Ethylene-α-olefin copolymers were synthesized using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing α-olefins and other polymerization conditions as shown in Table 28. Densities, intrinsic viscosities, and S.C.B. of these copolymers are shown in Table 28.

These copolymers are used in the following examples as higher molecular weight components.

EXAMPLE 46

Ethylene-α-olefin copolymers were synthesized using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing α-olefins and other polymerization conditions as shown in Table 29. Densities, intrinsic viscosities and S.C.B. of these copolymers are shown in Table 29.

These copolymers are used in the following examples as lower molecular weight components.

TABLE 28

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (kg)	C_2 partial pressure (kg/cm²)	Polymerization temperature (°C)	Properties: Density (g/cm³)	Properties: [η] (dl/g)	Properties: S.C.B.
A-1	Slurry	65	131	TEA 100	C_4 6.0	C'_4 6.14	0.45	5.0	50	0.899	2.6	38
A-2	"	65	145	TEA 50	"	"	0.59	6.7	50	0.906	2.6	29
A-3	"	65	310	TEA 100	"	"	0.70	7.8	50	0.912	2.6	24
A-4	"	65	125	"	"	"	1.8	18	50	0.923	2.6	9
A-5	Solution	1	25.3	DEAC 2.5	C_7 0.25	4-MP-1 0.11	0.1	20	140	0.904	2.5	23
A-6	Solution	1	24.5	"	C_7 0.30	4-MP-1 0.05	0.15	20	140	0.920	2.5	10
A-7	Slurry	65	121	TEA 50	C_4 6.0	C'_4 6.14	0.98	6.5	50	0.907	2.2	30
A-8	"	65	320	TEA 100	"	"	3.0	20	50	0.928	2.2	8

Note
TEA = Triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1 = 4-Methylpentene-1
C_4 = n-Butane
C'_4 = Butene-1
C_7 = n-Heptane

TABLE 29

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (kg/cm²)	C_2 partial pressure (kg/cm²)	Polymerization temperature (°C.)	Properties: Density (g/cm³)	Properties: [η] (dl/g)	Properties: S.C.B.
B-1	Slurry	65	405	TEA 50	C_6 50	C_4 2.0	10.8	8.3	70	0.912	0.83	15
B-2	"	65	411	"	C_6 15.2	C_4 1.6	6.5	5	70	0.935	0.83	20
B-3	"	65	402	"	C_6 12.0	C_4 3.2	7.8	6	70	0.929	0.85	24
B-4	"	65	408	TEA 100	"	C_4 4.0	5.2	4	50	0.910	0.82	35
B-5	Solution	1	26.5	DEAC 2.5	C_7 0.28	4-MP-1 0.03	3.0	10	140	0.938	0.50	13
B-6	"	1	25.7	"	C_7 0.25	4-MP-1 0.05	2.5	10	140	0.912	0.52	22
B-7	Slurry	65	407	TEA 100	C_6 15.4	C_4 0.5	13.0	5	70	0.953	0.62	9
B-8	"	65	422	TEA 50	C_6 15.2	C_4 1.8	11.0	5	70	0.934	0.61	22

Note
TEA = Triethyl aluminum
DEAC = Diethyl aluminum chloride
4-MP-1 = 4-Methylpentene-1
C_6 = n-Butane
C_4 = Butene-1
C_7 = n-Heptane

EXAMPLE 47

A composition of ethylene-α-olefin copolymers was prepared in two stage polymerization. The first stage polymerization was carried out for 70 min. using the catalyst produced in Example 1 and triethyl aluminum (co-catalyst) and other polymerization conditions as shown in Table 30. Successively, the second stage polymerization was conducted for 180 min. by changing only the hydrogen partial pressure and the ethylene partial pressure as shown in Table 30. In both stages, the liquid phase molar ratio of ethylene, butene-1 and hydrogen was kept constant at respective fixed levels. The polymerized quantities in each stage were calculated from the quantities of fed ethylene. The copolymer composition consisted of about 50% by weight of higher molecular weight components and about 50% by weight of lower molecular weight components. Immediately before the completion of the first stage polymerization, a part of the polymer was taken out and measured for its density, intrinsic viscosity and S.C.B. The whole polymer obtained after the second stage was also measured for the same test items. From the values of the first stage polymer and the whole polymer, the intrinsic viscosity and the number of branched short chains of the polymer formed in the second stage alone were calculated. These values were shown in Table 30. The whole polymer gave: density 0.921 g/cm³, MI 0.5 g/10 min., MFR 70, intrinsic viscosity 1.7 dl/g, S.C.B. 24, g_η^* 0.93. The whole polymer was subjected to gel permeation chromatography and a curve of molecular weight distribution shown in FIG. 4 was obtained.

Because of bimodal distribution which has two peaks, the curve was divided into two parts using broken lines. The areas of each part were calculated, and the lower molecular weight components and the higher molecular weight components were determined to be 48 and 52% by weight, respectively.

The whole polymer was divided into 30 fractions using column chromatography. These fractions were divided into two parts (the lower molecular weight components and the higher molecular weight components) so that the former became 48% by weight and the latter 52% by weight. S.C.B., densities and intrinsic viscosities of each component are shown in Table 32.

Flow characteristics and solid physical properties of the whole polymer are shown in Table 33.

In the following examples, ethylene-α-olefin copolymers as higher molecular weight components and ethylene-α-olefin copolymers as lower molecular weight components were mixed at respective fixed ratios (total quantity 1 kg) and kneaded for 5 min. with a Banbury mixer (150 to 230 rpm). At that time, replacement by nitrogen was conducted completely and the polymer temperatures were controlled not to exceed 250° C.

When sample quantities were small, mixing was made in xylene. After mixing, the whole solution was added into methanol to cause precipitation. After filtration, the precipitate was completely dried in a vacuum drier and used as a copolymers composition sample.

EXAMPLES 48, 49, 50

Ethylene-α-olefin copolymers obtained in Example 45 and ethylene-α-olefin copolymers obtained in Example 46 were kneaded with a Banbury mixer at ratios as shown in Table 31.

Thus, compositions of copolymers having densities, MIs, MFRs, intrinsic viscosities, S.C.B. and g_η^* shown in Table 32 were obtained. These compositions had molecular weight distribution curves about equal to FIG. 4. With the same technique as used in Example 47, quantities of lower molecular weight components and higher molecular weight components were calculated, and they were both approximately 50% by weight as shown in Table 32. Physical properties of these compositions are shown in Table 33.

With the same technique as used in Example 47, column fractionation was applied in order to divide into higher molecular weight components and lower molecular weight components. Characteristics of the components are shown in Table 32.

In Tables 32 and 33 are also shown Example 47 using a composition of ethylene-α-olefin copolymers prepared in two stage polymerization and, for comparison, Comparative example 26 using a high pressure method polyethylene of the conventional technique (commercial product Sumikathene ®F 101-1 manufactured by Sumitomo Chemical Co., Ltd.), Comparative example 27 using a composition of low density ethylene-α-olefin copolymers of the conventional technique and Comparative example 28 using a composition of low density ethylene-α-olefin copolymers of the conventional technique of which molecular weight distribution is made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B.

As is obvious from Tables 32 and 33, when compared with the high pressure polyethylene, the copolymer compositions of this invention have about equivalent Brabender torques (excellent in processability), and are largely excellent in tensile impact strength, rigidity, ESCR and tensile strength. Transparency is equally good, because distribution index of S.C.B. is in a certain range as defined by the present invention. When compared with the composition of low density ethylene-α-olefin copolymers of the conventional technique, the compositions of this invention have far smaller Brabender torques (much better processability) and higher tensile impact strengths and tensile strengths.

From comparison between Comparative examples 27 and 28 in Tables 32 and 33, it is learned that widening of molecular weight distribution (larger MFR gives wider distribution) in the manufacture of a low density ethylene-α-olefin copolymer of the conventional technique with density and MI fixed results in large reduction in tensile impact strength and tensile strength.

TABLE 30

No.	Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst TEA (mmol)	Solvent (g)	α-olefin (g)	H_2 partial pressure (kg/cm²)	C_2 partial pressure (kg/cm²)	Polymerization temperature (°C.)	Polymerization time (min)	Properties: Density (g/cm³)	Properties: [η] (dl/g)	Properties: S.C.B.
1st stage	Slurry	5	24.3	5	C_4 1000	C_4 250	0.6	4	50	70	0.912	2.6	24
2nd stage	Slurry						10	5		180	—	(0.8)	(23)

Note
C_4 = n-Butane
C_4 = Butene-1
C_2 = Ethylene
TEA = Triethyl aluminum
( ) = Calculated values

TABLE 31

	Higher molecular weight component: Designation	Higher molecular weight component: % by weight	Lower molecular weight component: Designation	Lower molecular weight component: % by weight
Example 48	A-1	50	B-1	50
Example 49	A-2	50	B-2	50
Example 50	A-3	50	B-3	50
Comparative Example 28	A-4	50	B-4	50

TABLE 32

	Properties of copolymer: Density (g/cm³)	MI (g/10 min.)	MFR	[η] (dl/g)	S.C.B.	g_η*	GPC: Length of main peak chain (A): Lower molecular weight component	GPC: Length of main peak chain (A): Higher molecular weight component	GPC: Ratio (% by weight): Lower molecular weight component	GPC: Ratio (% by weight): Higher molecular weight component
Example 47	0.921	0.5	70	1.7	24	0.96	1.7×10^3	3.4×10^3	48	52
Example 48	0.920	0.5	70	1.7	26	0.97	1.7×10^3	3.4×10^3	48	52
Example 49	0.920	0.5	70	1.7	25	0.93	1.6×10^3	3.5×10^3	47	53
Example 50	0.920	0.5	70	1.7	24	0.97	1.9×10^3	3.4×10^3	48	52
Comparative Example 26	0.922	0.3	65	1.06	23	0.48	1.05×10^3	6.5×10^3	36	64
Comparative Example 27	0.920	0.5	30	1.7	23	0.95	Uniform distribution (peak) 2.8×10^3		50	50
Comparative Example 28	0.920	0.5	70	1.7	22	0.95	1.6×10^3	3.6×10^3	49	51

	Characteristics of components fractionated by column fractionation: Lower molecular weight component: S.C.B.	Lower molecular weight component: Density (g/cm³)	Lower molecular weight component: [η] (dl/g)	Higher molecular weight component: S.C.B.	Higher molecular weight component: Density (g/cm³)	Higher molecular weight component: [η] (dl/g)	Distribution index of S.C.B.*
Example 47	30	0.920	0.8	18	0.915	2.6	0.6
Example 48	27	0.924	0.8	25	0.910	2.6	0.9
Example 49	28	0.923	0.7	20	0.914	2.5	0.7
Example 50	30	0.920	0.8	18	0.915	2.5	0.6
Comparative Example 26	27	0.916	0.6	19	0.926	1.4	0.7
Comparative Example 27	38	0.906	1.1	8	0.925	2.4	0.2
Comparative Example 28	37	0.907	0.8	7	0.926	2.6	0.2

*Distribution index of S.C.B. = $\frac{\text{Degree of S.C.B. of higher molecular weight component}}{\text{Degree of S.C.B. of lower molecular weight component}}$

TABLE 33

	Physical properties of copolymer						
	Tensile impact strength (kg-cm/cm²)	Olsen's Flexural modulus (kg/cm²)	Tensile strength (kg/cm²)	Haze (%)	Torque (kg-m)	ESCR F50 (hr)	Tackiness
Example 47	340	2600	280	5	2.0	>1000	o
Example 48	450	2600	320	20	2.0	>1000	o
Example 49	400	2700	300	8	2.0	>1000	o
Example 50	350	2800	280	5	2.0	>1000	o
Comparative Example 26	200	2200	190	6	2.2	30	o
Comparative Example 27	280	3200	260	8	3.5	>1000	o
Comparative Example 28	150	3300	210	12	2.0	>1000	x

EXAMPLES 51, 52

Compositions of ethylene-α-olefin copolymers were prepared by mixing ethylene-α-olefin copolymers obtained in Example 45 and ethylene-α-olefin copolymers obtained in Example 46 at ratios shown in Table 34. Densities, MIs, MFRs, [η], S.C.B. and g_η^* of these compositions are shown in Table 35. Their physical properties are shown in Table 36.

Molecular weight distributions of Examples 51 and 52 showed "one almost symmetrical mountain" curves. The curve in *FIG. 5 is that of Example 52.* Column fractionation was applied with the same technique as used in Example 47. Its results are shown in Table 35.

In Tables 35 and 36 are also shown low density ethylene-α-olefin copolymers of the conventional technique (Comparative examples 29 and 30) of which molecular weight distributions are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B.

Curves of molecular weight distributions of Comparative examples 29 and 30 were similar to those of Examples 51 and 52. As seen from Tables 35 and 36, in the compositions of this invention, S.C.B. of higher molecular weight components and those of lower molecular weight components are nearly equal (compare Example 51 with Comparative example 29, and also Example 52 with Comparative example 30), therefore, the compositions of the present invention are far superior to the copolymers of the conventional technique in tensile impact strength and tensile strength.

COMPARATIVE EXAMPLE 26

A commercial high pressure polyethylene (Sumikathene®F 101-1 manufactured by Sumitomo Chemical Co., Ltd.) was subjected to measurements of physical properties and. Results are shown in Table 33.

This polyethylene has low g_η^* of 0.48 and it suggests that this sample has many long chain branches. Its molecular weight distribution curve was shown in FIG. 6. Column fractionation was applied with the same technique as used in Example 47. The fractions obtained were divided into two groups so that the lower molecular weight component group and the higher molecular weight component group became about 36 and 64% by weight, respectively. Densities, S.C.B. and intrinsic viscosity of each group are measured and results were shown in Table 32.

COMPARATIVE EXAMPLE 27

A low density ethylene-α-olefin copolymer of the conventional technique was synthesized using the catalyst produced in Example 1, triethyl aluminum (cocatalyst) and other polymerization conditions as shown in Table 37. The copolymer gave: density 0.920 g/cm³, MI 0.5 g/10 min., MFR 30, intrinsic viscosity 1.7 dl/g, S.C.B. 23, g_η^* 0.95. Its physical properties are shown in Table 33. Its molecular weight distribution showed "one almost symmetrical mountain" curve, as seen in *FIG. 1. From the area ratio, the lower molecular* weight components and the higher molecular weight components were determined to be both 50% by weight. Column fractionation was applied with the same technique as used in Example 47 and results are shown in Table 32.

COMPARATIVE EXAMPLE 28

By mixing the ethylene-α-olefin copolymer A-4 obtained in Example 45 and the ethylene-α-olefin copolymer *B-4* obtained in Example 46 at the ratio as given in *Table 31, a composition of low density ethylene-α-ole*fin copolymers of the conventional technique was prepared of which molecular weight distribution is made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B. Its density, MI, MFR, [η], and g_η^* are shown in Table 32. The molecular weight distribution curve of this composition was *almost equal to that in FIG. 4.* With the same technique as used in Example 47, the ratio of the lower and higher molecular weight components was determined. Column fractionation was also conducted. These results are shown in Table 32. Physical proeprties of this composition are shown in Table 33.

COMPARATIVE EXAMPLES 29, 30

By mixing ethylene-α-olefin copolymers obtained in Example 45 and ethylene-α-olefin copolymers obtained in Example 46 at ratios as shown in Table 34, compositions of low density ethylene-α-olefin copolymers of the conventional technique were prepared of which molecular weigh. weight distributions are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B. Densities, MIs, MFRs, [η], S.C.B. and g_η^* of these compositions were shown in Table 35. Physical properties of these compositions were shown in Table 36.

TABLE 34

	Higher molecular weight component		Lower molecular weight component	
	Designation	% by weight	Designation	% by weight
Example 51	A-5	60	B-5	40
Example 52	A-7	50	B-7	50
Comparative Example 29	A-6	60	B-6	40
Comparative Example 30	A-8	50	B-8	50

REFERENCE EXAMPLE 1

An ethylene-α-olefin copolymer was synthesized from ethylene and butene-1, using the catalyst produced in Example 1, diethyl alminum monochloride (co-catalyst) and other polymerization conditions as shown in Table 38. Properties of this copolymer are shown in Table 39. By applying column fractionation, the copolymer was fractionated into fractions of different molecular weights. Then, distribution of S.C.B. against molecular weight was examined as shown in FIG. 7.

In column fractionation, about 5 g of the sample was placed in a fractionation column after being adsorbed on a carrier (Celite 745) in xylene. Then, the column was heated to 130° C., and butyl cellosolve and xylene were passed through the column with the mixing ratio being gradually changed in order to obtain a gradual increase in solvency. Thus, all the copolymer fractions of lower to higher molecular weight were separated. To the eluates was added methanol to cause precipitation of the copolymers. After recovery, the polymers were dried under reduced pressure and each copolymer fraction was obtained. In the above column fractionation process, in order to prevent the possible decomposition of the copolymers, 100 ppm of Irganox® 1076 was

TABLE 35

	Properties of copolymer						GPC: Length of main peak chain (Å)		GPC: Ratio (% by weight)	
	Density (g/cm³)	MI (g/10 min)	MFR	[η] (dl/g)	S.C.B.	g_η^*	Lower molecular weight component	Higher molecular weight component	Lower molecular weight component	Higher molecular weight component
Example 51	0.920	0.5	70	1.7	19	0.91	Uniform distribution (peak) 2.5×10^3		57	43
Example 52	0.929	1.2	70	1.4	20	0.95	Uniform distribution (peak) 1.6×10^3		48	52
Comparative Example 29	0.919	0.5	70	1.7	17	0.96	Uniform distribution (peak) 2.5×10^3		58	42
Comparative Example 30	0.929	1.2	70	1.4	17	0.93	Uniform distribution (peak) 1.6×10^3		48	52

	Characteristics of components fractionated by column fractionation						
	Lower molecular weight component			Higher molecular weight component			Distribution
	S.C.B.	Density (g/cm³)	[η] (dl/g)	S.C.B.	Density (g/cm³)	[η] (dl/g)	Index of S.C.B.*
Example 51	22	0.933	0.5	15	0.920	2.4	0.7
Example 52	20	0.935	0.6	20	0.915	2.2	1.0
Comparative Example 29	24	0.930	0.5	7	0.927	2.4	0.3
Comparative Example 30	29	0.922	0.6	6	0.930	2.1	0.2

*Distribution index of S.C.B. = $\frac{\text{Degree of S.C.B. of higher molecular weight component}}{\text{Degree of S.C.B. of lower molecular weight component}}$

TABLE 36

	Physical properties of copolymer			
	Tensile impact strength (kg · cm/cm²)	Olsen's Flexural modulus (kg/cm²)	Tensile strength (kg/cm²)	Tackiness
Example 51	480	2600	320	o
Example 52	250	3700	250	o
Comparative Example 29	200	3100	200	x
Comparative Example 30	70	4500	200	o

TABLE 37

Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst TEA (mmol)	Solvent (kg)	α-olefin (kg)	H_2 partial pressure (kg/cm²)	C'_2 partial pressure (kg/cm²)	Polymerization temperature (°C.)	Polymerization time (min)
Slurry	65	202	100	C_4 7.0	C'_4 7.16	3.0	10	50	90

Note
TEA = Triethyl aluminum
C_4 = n-Butane
C'_2 = Ethylene
C'_4 = Butene-1

added to the original sample and further air inside the column was replaced by nitrogen. Using each copolymer fraction, pressed sheets having about 100 to 300μ thickness were prepared, and S.C.B. of each copolymer fraction were calculated by conducting Fourier-transform infrared absorption spectroscopy. Molecular weights of each copolymer fraction were calculated, using intrinsic viscosities [η] measured in tetralin of 135° C. and the following formula.

$$[\eta] = 5.1 \times 10^{-4} \cdot M^{0.725}$$

REFERENCE EXAMPLE 2

With ethylene-α-olefin copolymers of the conventional technique, a relationship between melt index (MI) and tensile impact strength was examined with melt flow ratio (MFR) used as a parameter. Results were shown in FIG. 8. It is revealed that widening of molecular weight distribution results in remarkable reduction in tensile impact strength. (In the figure, molecular weight distribution was represented by MFR. Larger MFR means wider molecular weight distribution.). These ethylene-α-olefin copolymers were subjected to molecular weight fractionation with the same technique as used in Reference Example 1. All the copolymers showed trends similar to that of Reference Example 1. The fractions were divided into two groups (lower molecular weight group and higher molecular weight group) in such a way that each group became about 50% by weight, and (S.C.B. of higher molecular weight component/S.C.B. of lower molecular weight component) was calculated. It was below 0.5 in all the copolymers.

REFERENCE EXAMPLE 3

With a high pressure method polyethylene of the conventional technique and a linear, high density polyethylene of medium to low pressure method, correlations between melt index (MI) and intrinsic viscosity [η] were examined and are shown in FIG. 9. The correlation lines of each sample are clearly divided by a partition line (broken line). It is learned that the high pressure polyethylene has much lower intrinsic viscosity than that of the linear high density polyethylene of the same melt index.

A correlation between melt index and intrinsic viscosity was examined with the ethylene-α-olefin copolymers of the present invention. All of the copolymers of the present invention fell in the zone of the linear, high density polyethylene.

TABLE 38

Polymerization method	Polymerization vessel capacity (l)	Catalyst quantity (mg)	Solvent (g)	α-olefin (g)	H_2 partial pressure (kg/cm²)	C_2 partial pressure (kg/cm²)	Polymerization temperature (°C.)	Polymerization time (min)
Solution	1	25.1	C_7 300	C_4 40	3.5	20	140	90

TABLE 39

Properties			
Density (g/cm³)	MI (g/10 min)	MFR	S.C.B.
0.924	4	25	20

What is claimed is:

1. An ethylene-α-olefin copolymer composition excellent in transparency and strength and having a density of 0.915 to 0.929 g/cm³, a melt index of 0.02 to 50 g/10 min. and a melt flow ratio of 35 to 250, which comprises 10 to 70% by weight of an ethylene-α-olefin copolymer A and 90 to 30% by weight of an ethylene-α-olefin copolymer B; said copolymer A having a higher molecular weight than copolymer B and being a copolymer of ethylene and an α-olefin of 3 to 18 carbon atoms and having a density of 0.895 to 0.935 g/cm³, an intrinsic viscosity of 1.2 to 6.0 dl/g, the number of short chain branching per 1000 carbon atoms (hereinafter abbreviated as "S.C.B.") of 7 to 40 and a (weight average molecular weight)/(number average molecular weight) value of 2 to 10; said copolymer B being a copolymer of ethylene and an α-olefin of 3 to 18 carbon atoms and having a density of 0.910 to 0.955 g/cm³, an intrinsic viscosity of 0.3 to 1.5 dl/g, S.C.B. of 5 to 35 and a (weight average molecular weight)/(number average molecular weight) value of 2 to 10; said copolymer A and said copolymer B being selected in order to satisfy a condition that (S.C.B. of said copolymer A)/(S.C.B. of said copolymer B) is 0.6 to 1.7.

2. An ethylene-α-olefin copolymer composition according to claim 1, wherein at least one of said copolymer A and said copolymer B is an ethylene-butene-1 copolymer.

3. An ethylene-α-olefin copolymer composition according to claim 1, wherein at least one of said copolymer A and said copolymer B is an ethylene-4-methyl-pentene-1 copolymer.

4. An ethylene-α-olefin copolymer composition according to claim 1, wherein at least one of said copolymer A and said copolymer B is an ethylene-hexene-1 copolymer.

5. An ethylene-α-olefin copolymer composition according to claim 1, wherein at least one of said copolymer A and said copolymer B is an ethylene-octene-1 copolymer.

6. An extrusion processed material excellent in transparency and strength, obtained from an ethylene-α-olefin copolymer composition having a density of 0.915 to 0.929 g/cm³ and a melt index of 0.02 to 2.0 g/10 min. according to claim 1,2,3,4 or 5.

7. A film excellent in transparency and strength, obtained from an ethylene-α-olefin copolymer composition having a density of 0.915 to 0.929 g/cm³ and a melt index of 0.02 to 5 g/10 min. according to claim 1,2,3,4 or 5.

8. An injection molded material excellent in transparency and strength, obtained from an ethylene-α-olefin copolymer composition having a density of 0.915 to 0.929 g/cm³, a melt index of 2.0 to 50 g/10 min. and a melt flow ratio of 35 to 80 according to claim 1,2,3,4 or 5, which is obtained by mixing a copolymer A having an intrinsic viscosity of 1.2 to 4.0 dl/g and a copolymer B having a density of 0.910 to 0.950 g/cm³ and an intrinsic viscosity of 0.3 to 1.2 dl/g.

9. An ethylene-α-olefin copolymer composition according to claim 1,2,3,4 or 5, wherein said copolymer

composition is prepared by a multi-stage polymerization.

10. An ethylene-α-olefin copolymer composition according to claim 1,2,3,4 or 5, characterized in that said copolymer components are mixed as a result of a two stage polymerization wherein, in the first stage, said copolymer A is polymerized under certain polymerization conditions for a certain length of time and successively, in the second stage, said copolymer B is polymerized with the first stage polymerization conditions changed other than catalysts until an intended weight ratio of copolymers A and B is obtained.

11. An extrusion processed material according to claim 6, characterized in that said ethylene-α-olefin copolymer composition is obtained as a result of a multi-stage polymerization.

12. A film according to claim 7 characterized in that said ethylene-α-olefin copolymer composition is obtained as a result of a multi-stage polymerization.

13. An injection molded material according to claim 8, characterized in that said ethylene-α-olefin copolymer composition is obtained as a result of a multi-stage polymerization.

14. A composition of copolymers of ethylene and an α-olefin of 3 to 18 carbon atoms, having first and second component groups, said first component group having a higher molecular weight than said second component group, having the following properties:

(1) density of 0.915 to 0.929 g/cm^3,

(2) intrinsic viscosity [η] of 0.7 to 4.0 dl/g,

(3) melt index of 0.02 to 50 g/10 min.,

(4) S.C.B. being 5 to 45,

(5) $[\eta]/[\eta]_l$ namely g_η^* being at least 0.8, where $[\eta]_l$ is an intrinsic viscosity of a linear polyethylene having the same weight average molecular weight measured by a light scattering method,

(6) (S.C.B. of the first component group)/(S.C.B. of the second component group) being 0.6 to 0.8 where the two component groups are prepared by consolidating fractions obtained by column fractionation in two portions of lower and higher molecular weight components, said portions being selected so that the weight ratio of the two portions corresponds to the weight ratio of lower and higher molecular weight components calculated from the gel permeation chromotography curve,

(7) the second components have a density of 0.910 to 0.955 g/cm^3, an intrinsic viscosity of 0.3 to 1.5 dl/g and S.C.B. of 5 to 35,

(8) the first components have a density of 0.895 to 0.935 g/cm^3, an intrinsic viscosity of 1.2 to 6.0 dl/g and S.C.B. of 7 to 40, and

(9) the second components are 30 to 90% by weight and the first components are 70 to 10% by weight.

15. A copolymer composition according to claim 14 which gives at least a two-peak molecular weight distribution curve when subjected to gel permeation chromatography, in which curve the second component group contains at least one component having a peak chain length of 2×10^2 to 3.0×10^3 Å and the first component group contains at least one component having a peak chain length of 1×10^3 to 6×10^4 Å.

16. A copolymer composition according to claim 14, wherein said second components have S.C.B. of 5 to 35 and said first components have S.C.B. of 7 to 40.

17. A copolymer composition according to claim 14 which has a melt index of 0.04 to 10 g/10 min.

18. A copolymer composition according to claim 17 which has a melt flow ratio of 35 to 250.

19. A copolymer composition according to claim 18, wherein the α-olefin is butene-1.

20. A copolymer composition according to claim 18, wherein the α-olefin is 4-methylpentene-1.

21. A copolymer composition according to claim 18, wherein the α-olefin is hexene-1.

22. A copolymer composition according to claim 18, wherein the α-olefin is octene-1.

23. A copolymer composition according to claim 18 which is obtained from a multi-stage polymerization using a carrier-supported Ziegler catalyst.

* * * * *

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Naito et al.

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[54] ETHYLENE-ALPHA-OLEFIN COPOLYMER AND FILMS OBTAINED THEREFROM

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[51] Int. Cl.[5] B32B 27/32; C08L 23/08; C08F 210/02

[52] U.S. Cl. 428/523; 428/500; 525/240; 526/143; 526/348.3; 526/348.5; 526/348.6; 526/352.2

[58] Field of Search 526/143, 348.1, 348.5, 526/348.6, 348.3, 352.2; 525/240; 428/212, 218, 500, 523

[56] References Cited

U.S. PATENT DOCUMENTS

4,438,238 3/1984 Fukushima et al. 525/240

FOREIGN PATENT DOCUMENTS

1569833 6/1969 France 526/143
46-21212 6/1971 Japan 526/348.1
57-37616 8/1982 Japan 526/348.1
56-66405 4/1984 Japan 526/348.1
60-88016 5/1985 Japan 526/348.1

Primary Examiner—Fred Teskin
Attorney, Agent, or Firm—Saghrue, Mion, Zinn, Macpeak & Seas

[57] ABSTRACT

An ethylene-α-olefin copolymer comprising ethylene and an α-olefin having from 3 to 10 carbon atoms, the copolymer having an α-olefin content of from 1.0 to 8.0 mol %, a density of from 0.900 to 0.930 g/cm^3, and a melt flow rate of from 0.1 to 100 g/10 min., the programed-temperature thermogram of said copolymer as determined with a differential scanning calorimeter after being completely melted and then gradually cooled showing an endothermic peak (a) in a range of from 75° to 100° C. and an endothermic peak (b) in a range of from 120° to 140° C., with the ratio of an endotherm at the endothermic peak (b), ΔHb, to an endotherm at the endothermic peak (a), ΔHa, i.e., ΔHb/ΔHa, being from 0.03 to 2.0. The copolymer provides a film exhibiting excellent physical properties required for packaging film.

8 Claims, 6 Drawing Sheets

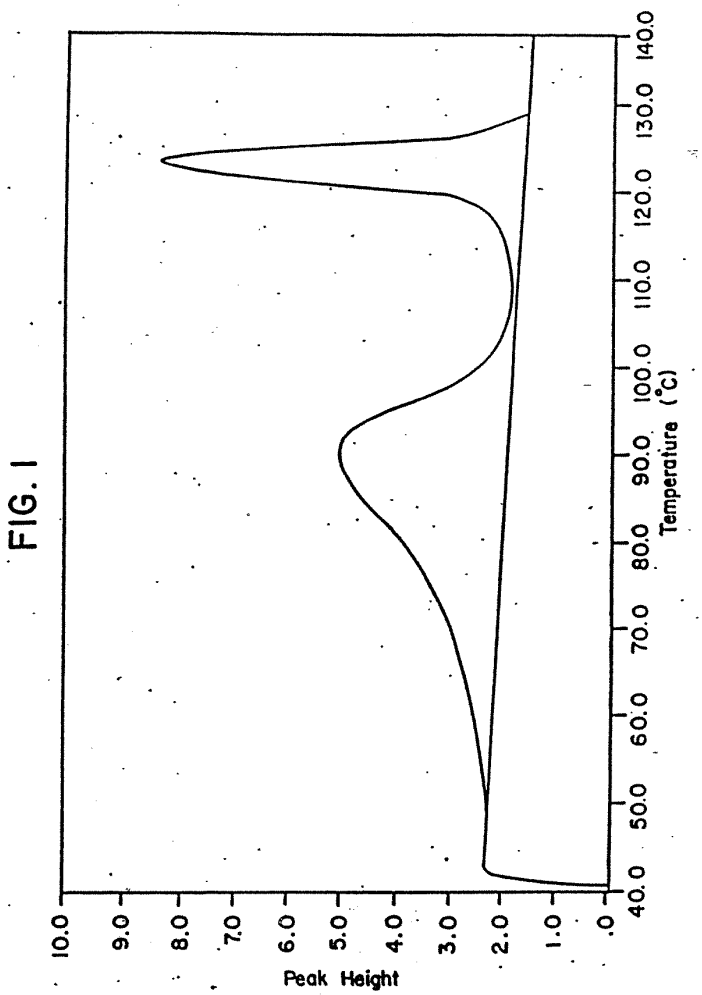


FIG. 1

EXHIBIT PAGE 000166

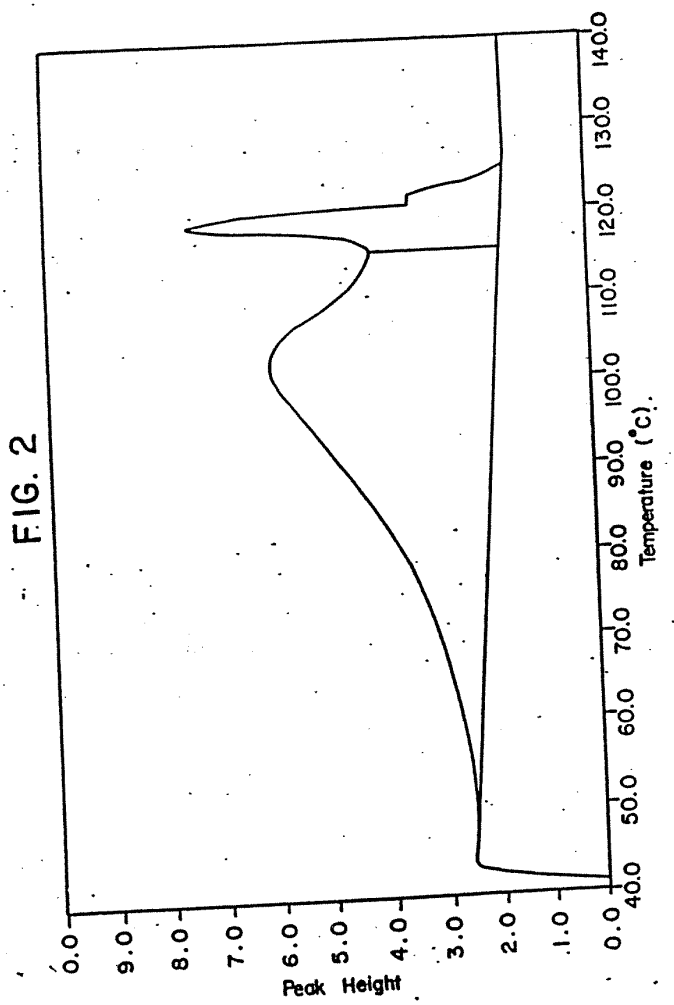

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Peak Height

FIG. 2

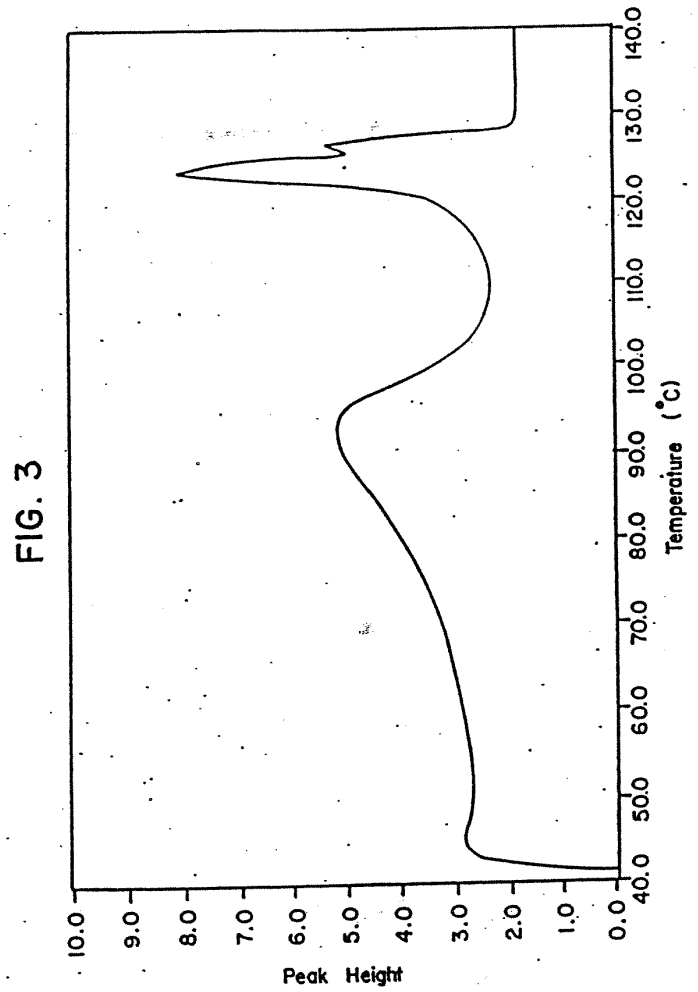

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Peak Height

FIG. 3

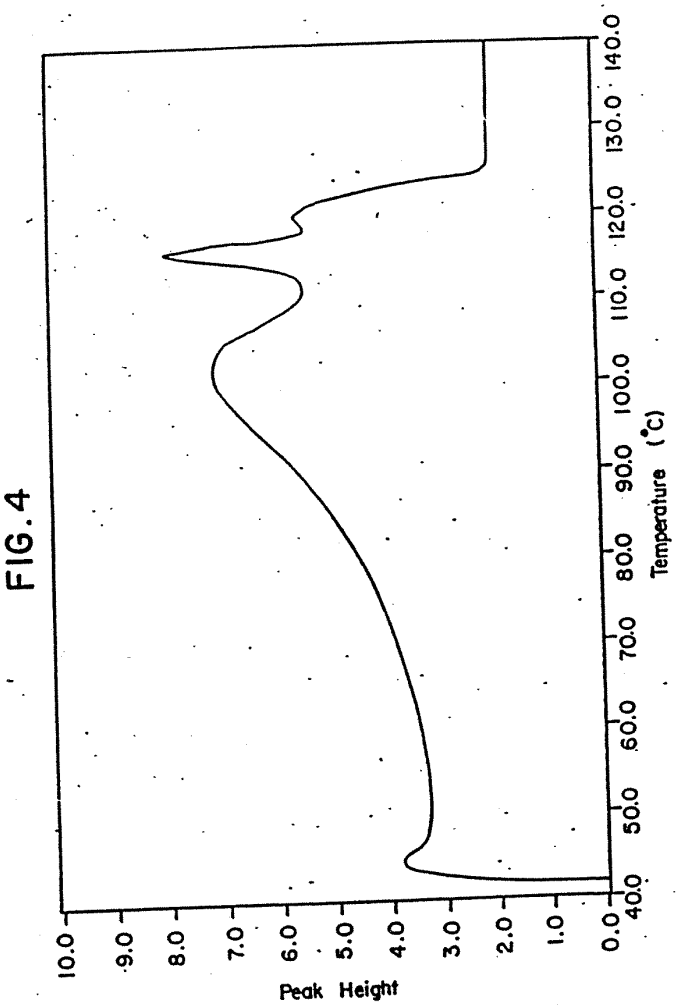


FIG. 4

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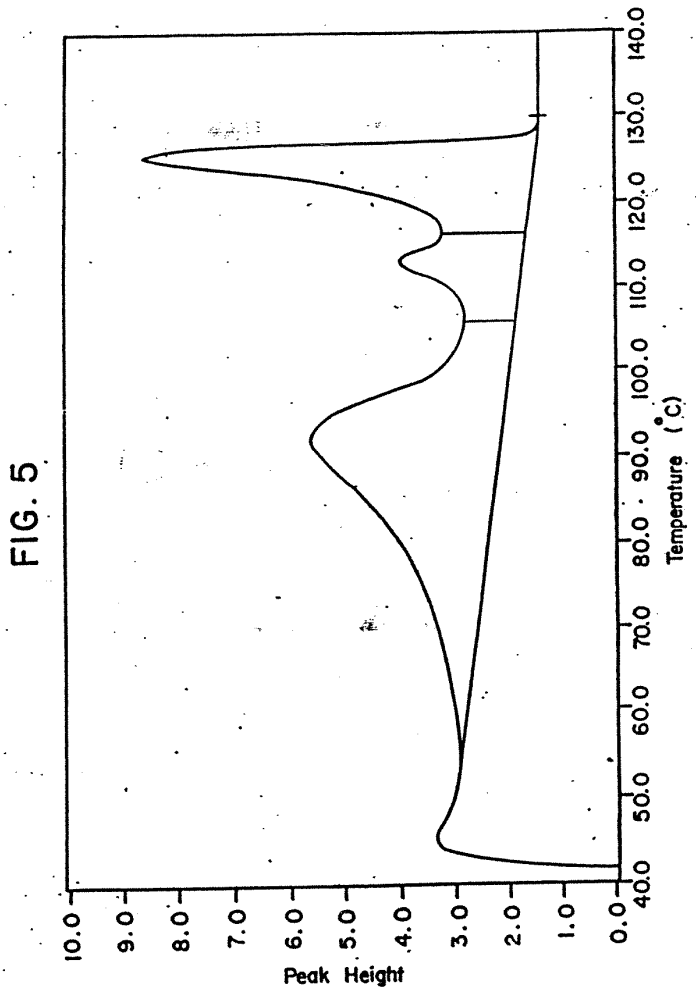

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FIG. 5

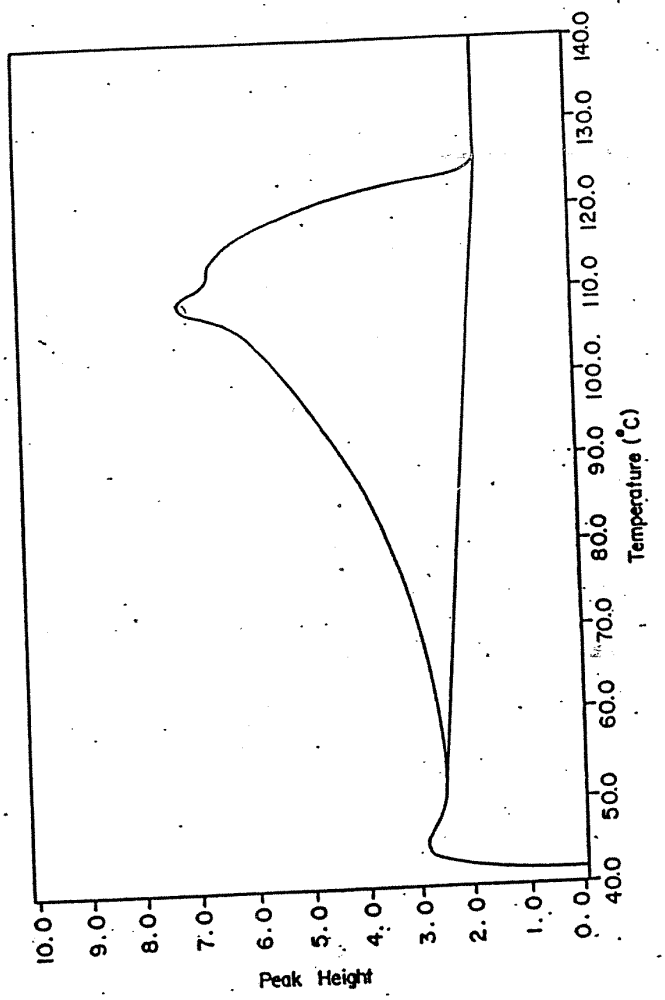

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Peak Height

FIG. 6

ETHYLENE-ALPHA-OLEFIN COPOLYMER AND FILMS OBTAINED THEREFROM

FIELD OF THE INVENTION

This invention relates to an ethylene-α-olefin copolymer, a low-density polyethylene film, and a polyethylene mixture. More particularly, it relates to an ethylene-α-olefin copolymer, a low-density polyethylene film, and a polyethylene mixture each of which highly satisfies performance properties required for use as packaging films, such as heat-sealing properties, transparency, gloss, nerve, impact strength, and tearing strength.

BACKGROUND OF THE INVENTION

Low-density polyethylene exhibits excellent water- and moisture-resistance, moderate softness, relatively good transparency, and relatively satisfactory strength and has therefore been used widely in the form of a film. In addition, since the low-density polyethylene is heat-sealable at temperatures of from a relatively low temperature and exhibits satisfactory heat-sealing strength, it is widespread as a single-layer packaging film or a packaging film laminate.

In recent years, a demand for a packaging film applicable to high-speed filling has been increasing. Speeding up of filling can be realized by speeding up of film delivery, reduction of heat-sealing time, and reduction of time of immediately from heat sealing to imposition of a load of a content on the sealed area. To this effect, a packaging film material is required to have nerve, to have low heat-sealing temperatures, and to exhibit satisfactory hot tack, i.e., to provide a sealed area that is not separated even when a load of a content is imposed thereon while being hot immediately after heat sealing. When composite films are produced by a lamination process, which is currently employed because it has a wide choice in the kind of film materials to be combined with and provides a composite film which can be beautifully printed, nerve of a low-density polyethylene film as a lamina is an important factor for achieving high-speed processing in that a lack of nerve easily causes wrinkles. Further, transparency and gloss are of importance for addition of a display effect to the content of package. Resistance to impact or tearing in any direction is also important as well for improving the essential packaging function of protection of the content.

Low-density polyethylene is divided into two large groups according to the process for production or molecular structure. One group is an ethylene polymer produced by free radical polymerization under high pressure and high temperature conditions, which essentially has short-chain branches and long-chain branches. It is considered that the short-chain branches and long-chain branches are formed through intramolecular rearrangement reaction and intermolecular rearrangement reaction, respectively, of a polymer radical under propagation. Since an α-olefin exhibits a high chain transfer constant in radical polymerization, it is present in a copolymerized state in high-molecular weight low-density polyethylene to be used as a synthetic resin in only a few proportion, if any. The other group is an ethylene-α-olefin copolymer produced by copolymerization in the presence of a transition metal catalyst, typically by a Ziegler process. By copolymerization with an α-olefin, short-chain branches whose carbon atom number is less than the α-olefin by two are formed, thereby decreasing the polymer density.

Generally having no long-chain branches, the latter polyethylene is called linear low-density polyethylene (L-LDPE). The former polyethylene has been simply called low-density polyethylene because it was invented before the latter, but will be hereinafter referred to as branched low-density polyethylene (B-LDPE) for distinction from L-LDPE.

In general, a high-molecular weight substance is a mixture of various molecules, and it is widely accepted that various physical properties very depending on a distribution mode of the molecules. Hence, analysis of the distribution mode, quantitative and structural elucidation of the relation between the distribution mode and various physical properties, and discoveries of high-molecular weight substances having a novel distribution mode and thereby exhibiting improved physical properties constitute one of the central subjects on high polymer science for both learning and industry.

With respect to low-density polyethylene, a molecular weight distribution and a distribution of short-chain branching coefficient are important factors for physical properties. It is known that B-LDPE has a broad molecular weight distribution and a relatively narrow short-chain branching coefficient distribution while L-LDPE generally has a relatively broad short-chain branching coefficient distribution as reported, e.g., in S. Hosoda, *Polymer J.*, Vol. 20, p. 383 (1988). Since the short-chain branching in L-LDPE arises through copolymerization of an α-olefin as a comonomer, the short-chain branching coefficient distribution of L-LDPE is sometimes referred to as a comonomer distribution or (copolymerization) composition distribution.

There is an extensive literature concerning the relationship between the composition distribution and physical properties in L-LDPE. JP-B-56-21212 (the term "JP-B" as used herein means an "examined Japanese publication") is one of the earliest literatures pointing the importance of comonomer distribution in partially crystalline ethylene-α-olefin copolymers. According to the disclosure, an extruded film of a copolymer having uniform comonomer distribution among molecules is superior to that of a non-uniform copolymer in terms of haze, impact strength, and balance of physical properties between the machine direction and the cross direction as demonstrated in the working examples in which films obtained by blow molding of uniform or non-uniform copolymers having a melt index of around 2 and a density of around 0.919 are evaluated for physical properties. The copolymers having a uniform comonomer distribution used therein are obtained by copolymerizing ethylene and an α-olefin in the presence of a catalyst prepared by mixing a specific organic aluminum compound and a specific vanadium compound. It is also disclosed in this reference that uniformity of comonomer distribution can be distinguished by a relationship between density and melting point of the copolymer as depicted by the accompanying drawing. That is, the density of the uniform copolymer is lower than that of the non-uniform copolymer having the same comonomer content. The reference nevertheless gives no description about heat-sealing properties and hot tack as important properties of a low-density polyethylene film. Neither does it refer to utility as composite films. As illustrated in the Comparative Examples of the present specification hereinafter described, a uniform copolymer has an extremely narrow range of heat-

sealing temperature within which satisfactory hot tack is obtained and is also insufficient in heat-sealability at low temperatures in spite of low rigidity. Notwithstanding the above-described relatively excellent properties, the uniform copolymer is of virtually no practical use as packaging film.

JP-A-59-66405 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") discloses that a copolymer film comprising ethylene and an α-olefin having 4 or more carbon atoms and having plural melting points exhibits excellent heat-sealability at low temperatures and still possesses high heat resistance. All the copolymers described in the working examples of this reference have three melting points but their maximum melting point does not exceed 124° C., with the minimum melting point being between 104° C. and 106° C. However, there is given no description of hot tack or utility as composite films.

JP-A-60-88016 describes that an ethylene-α-olefin random copolymer specified in composition distribution, branching coefficient distribution, randomness, DSC (differential scanning calorimetry) melting point, crystallinity, molecular weight distribution, etc. is excellent in mechanical characteristics, optical characteristics, anti-blocking properties, heat resistance, and low-temperature heat-sealability in a good balance. With respect to the composition distribution, it is made an essential condition that a composition distribution parameter derived from a specific means should not exceed a specific value, which condition means that the composition distribution must be sufficiently narrow. With respect to the DSC characteristics, it is essentially required that the maximum melting point should be in a specific range not high than 125° C.; the difference between the maximum melting point and the minimum melting point should be in a specific range; the difference between the maximum melting point and the second maximum melting point should be in a specific range; and the quantity of heat of crystal fusion at the maximum melting point is below a specific ratio to the total quantity of heat of crystal fusion. These essential requirements imply that the copolymer is the non-uniform copolymer as designated in JP-B-46-21212 but should be near to the uniform copolymer. It is also described that the film properties, such as low-temperature heat-sealability, would be reduced if the maximum melting point exceeds 125° C. or if the ratio of the quantity of heat of crystal fusion at the maximum melting point is too large. Moreover, there is found any description neither on hot tack nor on utility as composite films. Such an ethylene copolymer is unsatisfactory in film properties, such as low-temperature heat-sealability and hot tack, as shown in the Comparative Examples of the present specification hereinafter given.

Composition distribution is also changeable by uniformly mixing with an ethylene copolymer having a different comonomer content, inclusive of an ethylene homopolymer. In particular, an arbitrary composition distribution could be obtained, in principle, by mixing two or more uniform copolymers.

JP-B-57-37616 discloses a packaging polyolefin film comprising from 50 to 95 parts by weight, preferably from 70 to 90 parts by weight, of high-density polyethylene having a density of from 0.94 to 0.97 g/cm³ and from 5 to 50 parts by weight, preferably from 10 to 30 parts by weight, of a specific ethylene-1-butene random copolymer having a density of from 0.86 to 0.91 g/cm², preferably from 0.88 to 0.90 g/cm³, which is obtained by copolymerization in the presence of a vanadium catalyst. The film disclosed, however, has considerably higher nerve (rigidity) as compared with a film comprising B-LDPE and therefore cannot be referred to as a low-density polyethylene film. The reference also refers to a film obtained from a mixture containing an ethylene-1-butene random copolymer (density: 0.889 g/cm³) in a proportion higher than the above-specified range so as to exhibit rigidity equal to a B-LDPE film, but such a film suffers from blocking to an unmeasurable extent. It gives no specific description concerning heat-sealing properties, neither does it on hot tack.

In order to meet the recently increasing demand for rapid packaging, packaging films are essentially required to have excellent heat-sealing properties, and particularly hot tack. They are additionally required to have transparency and gloss for increasing display effects and high impact strength and tearing strength in any direction for protection of the content, a primary function for use as packaging material as stated above. However, none of the state-of-the-art low-density polyethylene films satisfies these physical properties inclusively.

SUMMARY OF THE INVENTION

One object of this invention is to provide a low-density polyethylene film which highly satisfies all the above-described physical requirements and is suitable for use as packaging film.

Another object of this invention is to provide a material from which the above-described low-density polyethylene film is produced.

The inventors extensively studied low-density polyethylene for use as packaging film and the mechanism of manifestation of heat-sealing properties, and particularly hot tack, that are of significance for the use. A heat sealing process comprises a heating step in which the temperature of a film is elevated by the heat from heat-sealing jaws previously heated to a prescribed temperature and a cooling step in which the sealed surface is relieved from the heat-sealing jaws and allowed to cool. The study has thus been centered on the relation between heat transfer behavior and heat-sealing properties and hot tack in low-density polyethylene. As a result, it has now been found that low-density polyethylene should exhibit a specific heat transfer behavior before highly excellent heat-sealing characteristics can be obtained. It has further been found unexpectedly that low-density polyethylene showing such a specific heat transfer behavior also satisfies other properties demanded for packaging films, such as transparency, gloss, nerve (rigidity), impact strength, and directionality of tearing strength.

That is, the present invention relates to an ethylene-α-olefin copolymer comprising ethylene and an α-olefin having from 3 to 10 carbon atoms, the copolymer having an α-olefin content of from 1.0 to 8.0 mol %, a density of from 0.900 to 0.930 g/cm³, and a melt flow rate (MFR) of from 0.1 to 100 g/10 min., the programed-temperature thermogram of said copolymer as determined with a differential scanning calorimeter (DSC) after being completely melted and then gradually cooled showing an endothermic peak (a) in a range of from 75° to 100° C. and an endothermic peak (b) in a range of from 120° to 140° C., with the ratio of an endotherm (ΔHb) at the endothermic peak (b) to an endotherm (ΔHb) at the endothermic peak (a), i.e., ΔHb/ΔHa, being from 0.03 to 2.0.

The present invention also relates to a film comprising the above-stated ethylene-α-olefin copolymer and a composite film containing said film on at least one side thereof.

The present invention further relates to a low-density polyethylene film whose programed-temperature thermogram as determined directly for the film state with a DSC shows an endothermic peak (a) in a range of from 75° to 100° C. and an endothermic peak (b) in a range of from 120° to 140° C., with the ΔHb/ΔHa ratio being from 0.03 to 2.0.

The present invention furthermore relates to a composite film containing the above-described low-density polyethylene film on at least one side thereof.

The present invention furthermost relates to a polyethylene mixture having a density of from 0.900 to 0.930 g/cm³ and an MFR of from 0.1 to 100 g/10 min., which comprises (I) from 60 to 99 parts by weight of an ethylene-α-olefin random copolymer comprising ethylene and an α-olefin having from 3 to 10 carbon atoms, the copolymer having an α-olefin content of from 2.0 to 10 mol% and a density of from 0.895 to 0.915 g/cm³, the programed-temperature thermogram of said copolymer as determined with a DSC after being completely melted and then gradually cooled showing an endothermic peak in a range of from 75° to 100° C., with the ratio of an endotherm at said peak to the total endotherm being at least 0.8, and (II) from 1 to 40 parts by weight of high-density polyethylene having a density of at least 0.945 g/cm³, the programed-temperature thermogram of said high-density polyethylene as determined with a DSC after being completely melted and allowed to cool showing an endothermic peak at 125° C. or higher [the sum of (I) and (II) amounts to 100 parts by weight].

The present invention additionally relates to a film comprising the above-described polyethylene mixture and a composite film containing said polyethylene mixture film on at least one side thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a programed-temperature thermogram of Example 2, which was determined after temperature reduction at a rate of 1° C./min followed by temperature rise at a rate of 10° C./min.

FIG. 2 is a programed-temperature thermogram of Comparative Example 4, which was determined after temperature reduction at a rate of 1° C./min followed by temperature rise at a rate of 10° C./min.

In FIGS. 1 and 2, the straight line nearly parallel to the abscissa (temperature) indicates a base line, and the line perpendicular to the abscissa indicates the temperature at which the thermogram reveals the minimum between endothermic peaks. An endotherm in each peak area is calculated by driwing a boundary at this point.

FIG. 3 is a programed-temperature thermogram of Example 2, which was determined after temperature reduction at a rate of 10° C./min followed by temperature rise at a rate of 10° C./min.

FIG. 4 is a programed-temperature thermogram of Comparative Example 4, which was determined after temperature reduction at a rate of 10° C./min followed by temperature rise at a rate of 10° C./min.

FIG. 5 is a programed-temperature thermogram of Example 2, which was determined directly from a film at a rate of temperature rise of 10° C./min.

FIG. 6 is a programed-temperature thermogram of Comparative Example 4, which was determined directly from a film at a rate of temperature rise of 10° C./min.

DETAILED DESCRIPTION OF THE INVENTION

As stated above, linear low-density polyethylene having a uniform or nearly uniform composition with a narrow composition distribution has been believed to provide a film excellent in transparency, impact strength, and low-temperature heat-sealing properties. In cases where the low-density polyethylene has plural melting points in thermal analysis with a DSC, it has been considered favorable to film properties that the maximum melting point should not be too high and the amount of heat of crystal fusion at the maximum melting point should be small. Unlike these received knowledges, the ethylene-α-olefin copolymer according to the present invention has a non-uniform composition distribution, and its maximum melting point is preferably as high as possible within a range permissible as polyethylene. As compared with the films obtained from the linear polyethylene based on the conventional concept, the film according to the present invention is characterized by strong nerve (high rigidity), excellent transparency and gloss, high impact strength, high tearing strength in both machine and cross directions, low heat-sealing temperature, and hot tack at low temperatures in a broad range. That is, the film of the invention is superior in all of the properties important as packaging film.

The ethylene-α-olefin copolymer which can be used in the present invention has a density of from 0.900 to 0.930 g/m³, preferably from 0.905 to 0.925 g/cm³, as measured after annealing at 100° C. for 1 hour in accordance with JIS K6760. While the film of the present invention exhibits strong nerve (i.e., high modulus) for the density of the ethylene-α-olefin copolymer used as a material, a density lower than the above-recited range results in production of a film of weak nerve, which tends to suffer from wrinkling on lamination. On the other hand, if the density is higher than that, the temperature at which heat-sealability or hot tack is manifested becomes too high to realize speeding up of packaging and filling.

The ethylene-α-olefin copolymer has an MFR of from 0.1 to 100 g/10 min. as measured according to JIS K6760. A preferred MFR varies depending on the process for producing films. For example, a preferred MFR is from 0.1 to 10 g/10 min., more preferably from 0.2 to 5 g/10 min., in the case of blown-film extrusion; from 0.5 to 50 g/10 min., more preferably from 1 to 10 g/10 min., in the case of T-die extrusion; or from 1 to 100 g/10 min., more preferably from 2 to 50 g/10 min., in the case of extrusion lamination. In general, according as an MFR decreases, the strength of the resulting film becomes higher but, in turn, the load of extrusion of film molding increases. According as an MFR increases, the film strength is reduced but it becomes easier to obtain a film of small thickness at a high speed.

The α-olefin to be copolymerized with ethylene contains from 3 to 10 carbon atoms as represented by formula:

$$R-CH=CH_2$$

wherein R represents an alkyl group having from 1 to 8 carbon atoms.

Specific examples of the α-olefin include propylene, butene-1, pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, 4-methylpentene-1, 4-methylhexene-1, and 4,4-dimethylpentene-1. Of these α-olefins, propylene produces relatively small improving effects, and those having 4 or more carbon atoms are preferred. In particular, butene-1, pentene-1, hexene-1, octene-1, and 4-methylpentene-1 are more preferred in view of availability and quality of the resulting copolymers. If desired, these α-olefins may be used in combination of two or more thereof.

The most important factor in the present invention is a thermal transition behavior as hereinafter described. AS is commonly accepted, a thermal transition behavior of a polymer can be determined with a DSC. A diagram of exothermic or endothermic reaction rate vs. temperature, called a thermogram, reflects a distribution of lamella thickness of the polymer. The lamella thickness distribution is known to be influenced by the composition distribution and thermal history of the polymer as described, e.g., in S. Hosoda, *Polymer J.*, Vol. 20, p. 383 (1988).

Determination of thermal transition behavior as referred to in the present invention is divided into two cases, one for obtaining information regarding composition distribution of a polymer per se, and the other for obtaining information regarding lamella thickness distribution of a film obtained from the polymer.

In the former case, a programed-temperature thermogram is determined after a polymer is completely melted and then gradually cooled. Since the thermal transition behavior of polymers changes according to their thermal history, the determination should be done after removing the influences of the thermal history. As shown in the accompanying drawings and Reference Examples hereinafter described, if the rate of cooling is not sufficiently low, a seeming splitting of the peak may sometimes be found in the subsequent temperature rise. This is probably because lamellar crystals which have not been allowed to sufficiently grow under rapid cooling undergo fusion-recrystallization during the temperature rise. Hence, in the present invention, a sample is kept in a DSC at 150° C. for 5 minutes (premelting) and then cooled to 40° C. at a rate of 1° C./min to obtain a thermogram under temperature drop and, thereafter, the sample is heated up to 150° C. at a rate of 10° C./min to obtain a thermogram under temperature rise. In each thermogram obtained, a straight line is drawn between the point at which heat generation initiates and the point of 50° C. or between the point of 50° C. and the point at which the endothermic reaction comes to the end. This line is a base line for calculating amounts of heat. The terminology "peak" as used herein means one revealing a clear maximum in endothermic side excluding a shoulder merely discernible by an inflection point or a mountain looking like a peak due to a small change of less than 1/10 the maximum peak intensity. In other words, minute changes of a thermogram are of no concern of the present invention.

What is important for the ethylene-α-olefin copolymer of the present invention is that its programed-temperature thermogram reveals an endothermic peak (a) in a temperature range of from 75° to 100° C., preferably from 80° to 95° C. The thermogram may have plural endothermic peaks (a) within the above-recited temperature range. If the peak temperature of the endothermic peak (a) is higher than 100° C., the resulting film fails to exhibit heat-sealability and hot tack from a sufficiently low temperature. If it is lower than 75° C., the resulting film has reduced heat-sealing properties or a reduced maximum peel strength while hot-tack.

It is also necessary that the programed-temperature thermogram should also have an endothermic peak (b) at 120° C. or higher. If there is only the endothermic peak (a), the temperature at which hot tack and heat-sealability can be manifested is not sufficiently lowered. Besides, the temperature range in which hot tack is exhibited is extremely narrow, making the film virtually useless.

In order to enjoy heat-sealability and hot tack from a sufficiently low temperature, a ratio of an endotherm (ΔHb) at the peak (b) to an endotherm (ΔHa) at the peak (a), i.e., a ΔHb/ΔHa ratio, should be at least 0.03, preferably 0.05 or more, more preferably 0.10 or more. On the other hand, if the ΔHb/ΔHa ratio is larger than 2.0, the temperature at which hot tack and heat-sealability are exhibited becomes unfavorably high. Accordingly, the ΔHb/ΔHa ratio should not exceed 2.0, preferably not exceed 1.5, more preferably not exceed 1.0. If the temperature at the endothermic peak (b) is lower than 120° C., the temperature range for manifestation of hot tack becomes narrow. A preferred endothermic peak (b) is present at 122° C. or higher. From the fact that the melting point of polyethylene does not exceed 140° C., the peak temperature of the endothermic peak (b) is not higher than 140° C. Plural endothermic peaks (b) may be present within the above-recited temperature range.

The endotherm ΔHa is a quantity of heat of absorption is the peak area between temperatures at each of which the thermogram falls to the minimum (the endothermic side being taken as positive) between endothermic peaks each observed in the higher or lower temperature side than the range in which the endothermic peak (a) should be present. In case where no endothermic peak is observed in the lower temperature side, the level at 50° C. is used as a boundary. The endotherm ΔHb is a quantity of heat of absorption in the peak area between a temperature at which the thermogram falls to the minimum between the endothermic peak (b) and an endothermic peak observed in the lower temperature side than the range in which the endothermic peak (b) should be present and a temperature at which endothermic reaction comes to an end. In case where a given minimum level is maintained over a certain temperature range, the central temperature in that range is taken as a boundary.

Although the programed-temperature thermogram of the ethylene-α-olefin copolymer according to the present invention may have endothermic peaks other than the above-described peaks (a) and (b), it is preferable for obtaining the full effects of the present invention that the ratio of the sum of ΔHa and ΔHb to the total endotherm ΔHt, i.e., (ΔHa+ΔHb)/ΔHt, is at least 0.7, more preferably at least 0.8, most preferably at least 0.9.

The endothermic peak (a) preferably has a half width ($W_{a\frac{1}{2}}$) of not more than 30° C., more preferably not more than 27° C., most preferably not more than 25° C. $W_{a\frac{1}{2}}$ is a temperature difference between two intersections of (i) the line extending from the middle point of a perpendicular drawn from the peak (a) down to the base line in parallel to the base line and (ii) the thermogram. In cases where the line (i) intersects the borderline from the neighboring peak before intersecting the thermogram, $W_{a\frac{1}{2}}$ is a temperature difference between the temperature at this intersection and the other intersection. If $W_{a\frac{1}{2}}$ exceeds 30° C., the heat-sealing

strength or peel length while hot-tack in a low temperature side becomes unfavorably high.

When the thermal transition behavior is determined for obtaining information about lamella thickness distribution of a film obtained from the low-density polyethylene, a programed-temperature thermogram is obtained using the polyethylene in the form of a film.

The crystal fusion behavior of a molded article is decided not only by a composition distribution of the starting polymer per se but by thermal history of the molded article during or after processing. Therefore, when it is intended to know the heat fusion behavior of the film of itself, it is necessary to determine the thermogram without subjecting the film to any thermal treatment prior to the determination. In the present invention, accordingly, the film is placed in a DSC measuring pan and heated from 40° C. to 150° C. at a rate of 10° C. per minute to obtain a programed-temperature thermogram. The resulting thermogram is analyzed for temperature, quantity of heat, and half width of the fusion peaks in the same manner as described above. In this case, however, since the lamella thickness distribution assigned to the thermal history carries weight, any change of 5% or more of the maximum peak intensity of the thermogram is regarded as a peak.

Films obtained from the conventional L-LDPE by the molding methods hereinafter described have a programed-temperature thermogram showing an essentially single broad endothermic peak, whereas the films of the present invention are characterized by their programed-temperature thermogram showing plural clear endothermic peaks as illustrated below.

The programed-temperature thermogram of the polyethylene film according to the present invention is required to have an endothermic peak (a) in a range of from 75° to 100° C., preferably from 80° to 95° C. The thermogram may have two or more endothermic peaks (a) within the above-specified range. If the near temperature of the endothermic peak (a) is higher than 100° C., sufficient heat-sealability and hot tack cannot be exerted from a low temperature.

The programed-temperature thermogram of the polyethylene film should also have an endothermic peak (b) in a temperature range of 120° C. or higher. If there is only the endothermic peak (a), the temperature at which hot tack and heat-sealability can be manifested is not sufficiently lowered and, in addition, the temperature range in which hot tack is exhibited is extremely narrow, making the film virtually useless.

In order to enjoy heat-sealability and hot tack from a sufficiently low temperature, a ratio of an endotherm (ΔHb) at the peak (b) to an endotherm (ΔHa) at the peak (a), i.e., a $\Delta Hb/\Delta Ha$ ratio, should be at least 0.03, preferably 0.05 or more, more preferably 0.10 or more. On the other hand, if the $\Delta Hb/\Delta Ha$ ratio is larger than 2.0, the temperature at which hot tack and heat-sealability are exhibited becomes unfavorably high. Accordingly, the $\Delta Hb/\Delta Ha$ ratio should not exceed 2.0, preferably not exceed 1.5, more preferably not exceed 1.0. If the temperature at the endothermic peak (b) is lower than 120° C., the temperature range for manifestation of hot tack becomes narrow. A preferred endothermic peak (b) is present at 122° C. or higher. From the fact that the melting point of polyethylene does not exceed 140° C., the peak temperature of the endothermic peak (b) is not higher than 140° C. Plural endothermic peaks (b) may be present within the above-recited temperature range.

Although the programed-temperature thermogram of the polyethylene film may have endothermic peaks other than the above-described peaks (a) and (b), it is preferable for obtaining the full effects of the present invention that the ratio of the sum of ΔHa and ΔHb to the total endotherm ΔHt, i.e., $(\Delta Ha+\Delta Hb)/\Delta Ht$, is at least 0.6, more preferably at least 0.7, most preferably at least 0.75.

The endothermic peak (a) of the polyethylene film preferably has a half width (Wa_{178}) of not more than 27° C., more preferably not more than 25° C., most preferably not more than 23° C. Wa_{178} is a temperature difference between two intersections of (i) the line extending from the middle point of a perpendicular drawn from the peak (a) down to the base line in parallel to the base line and (ii) the thermogram. In cases where the line (i) intersects the borderline from the neighboring peak before intersecting the thermogram, Wa_{178} is a temperature difference between the temperature at this intersection and the other intersection. If Wa_{178} exceeds 27° C., the heat-sealing strength or peel length while hot-tack in a low temperature side becomes unfavorably high.

The ethylene-α-olefin copolymer according to the present invention can be synthesized by copolymerizing ethylene and an α-olefin having from 3 to 10 carbon atoms in a polymerization vessel. In one example of the synthesis, the ethylene-α-olefin copolymer of the present invention can be obtained by polymerizing ethylene in the presence of a catalyst composed of (a) a transition metal component and (b) an organometallic compound and then feeding an α-olefin and (c) a third component to the polymerization system. The density and α-olefin content of the ethylene-α-olefin copolymer can be controlled by adjusting the amounts of the α-olefin and the third component (c) to be fed. Since these amounts depend on the kinds of the components (a), (b), and (c), the polymerization temperature, and the polymerization pressure, they should be experimentally determined as specifically shown in the Examples hereinafter described.

The polyethylene mixture according to the present invention can be obtained by mixing (I) from 60 to 99 parts by weight of a random copolymer comprising ethylene and an α-olefin having from 3 to 10 carbon atoms and having a density of from 0.895 to 0.915 g/cm^3, preferably from 0.900 to 0.910 g/cm^3, and an α-olefin content of from 2.0 to 10.0 mol %, the DSC programed-temperature thermogram of which reveals an endothermic peak in a range of from 75° to 100° C., preferably from 80° to 95° C., with the ratio of an endotherm at the peak to the total endotherm being at least 0.8, and (II) from 1 to 40 parts by weight of high-density polyethylene having a density of at least 0.945 g/cm^3, the DSC programed-temperature thermogram of which reveals an endothermic peak at 125° C. or higher, preferably 130° C. or higher, wherein the sum of the copolymer (I) and the high-density polyethylene (II) amounts to 100 parts by weight.

The copolymer (I) can be obtained by the process disclosed in Japanese Patent Application No. 63-142522 applied by Sumitomo Chemical Co., Ltd. More specifically, the process comprises copolymerizing ethylene and an α-olefin having from 3 to 10 carbon atoms in a hydrocarbon solvent in the presence of a catalyst system composed of (a) a vanadium compound represented by formula:

$VO(OR)_nX_{3-n}$

wherein R represents a hydrocarbon group; X represents a halogen atom; and $0<n<3$, as a transition metal component, (b) an organoaluminum compound represented by formula:

R'_mAlX_{3-m}

wherein R' represents a hydrocarbon group; X represents a halogen atom; and $1<m<3$, as an organometallic component, and (c) an ester compound (hereinafter referred to as M) represented by formula:

$R''(C=O)OR'''$

wherein R'' represents an organic group having from 1 to 20 carbon atoms whose hydrogen atoms are partly or totally substituted with a halogen atom; and R''' represents a hydrocarbon group having from 1 to 20 carbon atoms, at an Al/V molar ratio of at least 2.5 and an M/V molar ratio of at least 1.5, at an ethylene/α-olefin molar ratio of from 35/65 to 60/40 at a polymerization temperature of from 40° to 80° C. in such a system wherein a hydrocarbon solvent-insoluble polymer (slurry phase) and a hydrocarbon solvent-soluble polymer (solution phase) coexist.

The copolymer (I) can also be obtained by the process disclosed in JP-A-60-226514, in which copolymerization is carried out in the same manner as described above, except for using a vanadium compound prepared by reacting vanadium trichloride and an alcohol as the transition metal component (a). The copolymer (I) may also be obtained by the process described in JP-B-46-21212.

The α-olefin to be used preferably contains from 4 to 10 carbon atoms. In using α-olefins having 6 or more carbon atoms, the polymerization is preferably effected by using the above-described vanadium compound according to JP-A-60-226514.

The high-density polyethylene (II) is an ethylene homopolymer and/or a copolymer of ethylene and an α-olefin having from 3 to 10 carbon atoms and is selected from those commercially available as high-density polyethylene.

The MFR of each of the copolymer (I) and the high-density polyethylene (II) is arbitrarily selected from a range of from 0.01 to 1000 g/10 min. as far as the MFR of the mixture thereof falls within a rang of from 0.1 to 100 g/10 min. In selecting the MFR, the fact that MFR logarithms substantially have an additive property can be made a guide.

A weight mixing ratio of the copolymer (I) to the high-density polyethylene (II) preferably ranges from 98/2 to 70/30, more preferably from 97/3 to 80/20.

The copolymer (I) and the high-density polyethylene (II) are blended at temperatures above the point at which both of them are fused to obtain a uniform mixture. Blending can be carried out with any of known kneading machines, either batch or continuous types or single- or multi-screw types, as well as an extruder of a film producing apparatus.

The polyethylene film according to the present invention can be produced from the above-described ethylene-α-olefin copolymer or polyethylene mixture at a temperature of fusing the resins by known techniques, such as inflation, T-die extrusion, etc.

The inflation is called blown-film extrusion and comprises extruding a molten resin from an extruder through a circular slit of a ring die and blowing a gas (usually air) into the inside of the extruded tubular film at a controlled blow pressure to obtain a film having a broad range of width. The ratio of the diameter of the blown tubular film to the diameter of the circular slit is called a blow-up ratio (BUR). The film thickness can be adjusted by selecting the extrusion rate and BUR. The extruded and blown tubular film is cooled with a gas (usually air) and/or a liquid (usually water) from the outside. The technique including cooling with water, called water-cooling inflation, is useful for producing films having excellent transparency but a thickness alteration is troublesome to make. On the other hand, various devices and methods for cooling in the technique including cooling with air, called air-cooling inflation have been proposed. The air-cooling inflation is divided into a single-stage air-cooling system and a multi-stage air-cooling system. Since conventional films produced by single-stage air-cooling inflation of L-LDPE exhibit insufficient transparency, the multi-stage air-cooling system was proposed to solve this problem. The latter system, however, involves difficulty in altering a film thickness similarly to the water-cooling inflation technique and hence loses the merit of inflation that a plural kind of films can be produced in the same machine.

The ethylene-α-olefin copolymer or polyethylene mixture according to the present invention provides films having very excellent transparency even by the single-stage air-cooling inflation. It is a matter of course that films excellent in transparency can also be obtained by water-cooling inflation or multi-stage air-cooling inflation as well. The resin temperature on film extrusion is usually selected from the range of from a complete fusion temperature to 250° C.

T-die extrusion is called a cast film process, in which a resin kneaded and melted in an extruder is extruded through a parallel slit of a lot die and cooled on contact with a chill roll through which a cooling medium such as water is circulated to obtain films generally excellent in transparency and thickness accuracy. The thickness of the case film can be adjusted by selecting a rate of extrusion and a take-off speed. The resin temperature on casting is usually selected from the range of from a complete fusion temperature to 350° C.

A single-layer film comprising the low-density polyethylene of the present invention usually has a thickness of from 5 to 500 μm, preferably from 10 to 100 μm. If the film thickness is less than 5 μm, processing becomes difficult and also handling of the film on lamination becomes difficult. If the thickness is too large, not only processing becomes difficult but heat-sealing properties are hardly manifested.

For making the full advantage of the superior heat-sealing properties of the film according to the present invention, it is desirable that the low-density polyethylene film of the invention be combined with other bases in the form of a composite film, in which the low-density polyethylene film preferably constitutes a surface layer on at least one side thereof.

The bases to be combined can be selected arbitrarily from among film-forming polymers, cellophane, paper, paperboard, fabric, an aluminum foil, and the like. The film-forming polymers include polyamide resins, e.g., nylon 6, nylon 66, nylon 11, and nylon 12; polyester resins, e.g., polyethylene terephthalate and polybutylene terephthalate; polyolefin resins, e.g., polypropyl-

ene, poly-1-butene, poly-4-methyl-1-pentene, polyethylene, an ethylene-vinyl acetate copolymer, an ethylene-methacrylate copolymer, an ethylene-acrylate copolymer, an ethylene-methacrylic acid copolymer, and ionomers; polyvinylidene chloride; polyvinyl chloride; polystyrene; polyvinyl alcohol; an ethylene-vinyl alcohol copolymer; etc. These film-forming polymers can be chosen according to the end use of a composite film taking into consideration gas barrier properties, printability, transparency, rigidity, adhesion, or the like factor. In cases of using stretchable bases, particularly those which are stretched to provide improved film characteristics, such as polyamide resins, polyester resins, and polypropylene, the base may be uniaxially or biaxially stretched, if desired.

In composite films, the low-density polyethylene film layer of the present invention usually has a thickness of from 1 to 500 μm, preferably from 10 to 100 μm. The thickness of the base is arbitrary and can be decided depending on the end use. It is widespread to produce a composite film containing plural bases in various layer structures, and such a technique is applicable to the present invention.

The composite films composed of two or more layers can be produced by known processes, such as lamination processes including dry lamination, wet lamination, sandwich lamination, and hot-melt lamination; co-extrusion, extrusion coating (called extrusion lamination), and a combination thereof.

According to the lamination process, the film of the present invention obtained by the above-described process or the composite film herein described is laminated with other base using a solvent type adhesive, an aqueous adhesive, a hot-melt adhesive, a molten polymer, etc. In the co-extrusion process, the low-density polyethylene of the present invention and other polymer are separately melted and extruded and brought into contact with each other in the inside and/or outside of an extrusion die. In the extrusion coating process, the low-density polyethylene film of the present invention or a molten polymer film obtained by the above-described co-extrusion is coated on at least one side of a base or the composite film herein described. For the detailed information about these processes, reference can be made to it in *Laminate Kako Binran*, published by Kako Gijutsu Kenkyukai.

Of the thus produced composite films, those having a uniaxially or biaxially stretchable base may be subjected to uniaxial or biaxial stretching. Stretching would provide a stretched composite film having its low-density polyethylene layer reduced to a thickness of about 1 μm. The stretching of the composite film can be carried out under heating to a temperature at which the base used can be stretched by any known technique, such as tentering, inflation, and rolling. If desired, the stretched composite film may be subjected to heat setting.

If desired, the film or mixture according to the present invention can contain various known additives such as antioxidants, weathering agents, lubricants, anti-block agents, antistatic agents, anti-fogging agents, anti-water drop agents, pigments, and fillers.

The film according to the present invention exhibits excellency in all the properties required for use as packaging film. That is, it has strong nerve (high rigidity), excellent transparency and gloss, high impact strength, and well-balanced tearing strength in the machine and cross directions and exhibits heat-sealability at low temperatures and hot tack at low temperatures of a broad range. Therefore, the film, either in the form of a single-layer film or a composite film, can be used for packaging a wide variety of contents, such as foods to be packed together with water; liquid foods, e.g., milk and soups; dry foods, e.g., confectionary; processed meat products, e.g., ham and sausage; and so on.

The present invention is now illustrated in greater detail by way of the following Examples, Comparative Examples, and Reference Example, but it should be understood that the present invention is not deemed to be limited thereto.

In these example, physical properties were measured by evaluated according to the following methods.

(1) Density

Measured in accordance with JIS K6760. The measurement was conducted after subjecting a sample to annealing in water at 100° C. for 1 hour.

(2) MFR

Measured in accordance with JIS K6760.

(3) DSC Thermogram

Determined with a differential scanning calorimeter, DSC-7 manufactured by Perkin-Elmer Corporation.

(i) Determination of programed-temperature thermogram after complete fusion followed by gradual cooling

A specimen weighing about 10 mg cut out of an about 0.5 mm thick pressed sheet is put in a sample pan of a DSC, premelted at 150° C. for 5 minutes, cooled to 40° C. at a rate of 1° C./min, and kept at that temperature for 5 minutes. Thereafter, the specimen is heated up to 150° C. at a rate of 10° C./min to obtain a thermogram.

(ii) Determination of programed-temperature thermogram directly for film

Several laid-up films totally weighing about 10 mg are put in a sample pan of a DSC and kept at 40° C. for 5 minutes. Thereafter, the films are heated up to 150° C. at a rate of 10° C./min to obtain a thermogram.

(4) Haze (Degree of Cloudiness)

Measured in accordance with ASTM D1003. The smaller the measured value, the higher the transparency.

(5) Gloss

Measured in accordance with JIS Z8741. The greater the value obtained, the higher the gloss.

(6) Secant Modulus at 1% Strain

A 2 cm wide specimen cut out of a film in the machine direction (MD) or the cross direction (CD) is fixed to a tensile tester at a chuck distance of 6 cm and pulled at a speed of 5 mm/min. The secant modulus can be calculated by inserting a stress at 1% elongation into formula [100×(stress)/(cross sectional area)].

(7) Dart Drop Impact Strength

Measured according to ASTM D1709, Method A.

(8) Elmendorf Tear Strength

Measured according to JIS Z1702.

(9) Heat-Sealing Properties

Two composite films are contacted in such a manner that the polyethylene layers face to each other and heat sealed to a width of 10 mm by means of a heat sealer manufactured by Tester Sangyo K.K. under a jaw pressure of 1.0 kg/cm² for a heat-sealing time of 1.0 second, with a heat-sealing temperature being varied from 85° C. to 150° C. by 5° C. The sealed film is cut to a width of 15 mm in the direction at right angles to the sealed area and a peel strength of the sealed area is measured with a Schopper tensile tester at a peel angle of 180° and at a pulling speed of 200 mm/min.

(10) Hot Tack

Two 15 mm-wide composite films are contacted in such a manner that the polyethylene layers face to each other, and a load of 30 g is applied on one of the films via a pulley. The films are heat sealed to a width of 20 mm by means of a heat sealer manufactured by Tester Sangyo K.K. at a jaw pressure of 1.3 kg/cm² for a sealing time of 0.3 second with a jaw temperature (heat sealing temperature) being varied from 100° C. to 170° C. by 5° C. In the instant of completion of heat sealing, the load is dropped thereby applying a peel force due to the load on the sealed surface in 0.14 second from the completion of heat sealing. The length actually peeled apart (peel length) is measured.

In the following description, all the parts and percents are given by weight unless otherwise indicated.

EXAMPLES 1 TO 11 AND COMPARATIVE EXAMPLES 1, 2, 5 AND 7

(1) Preparation of Copolymer (I)

To the lower part of a 200 l-volume jacketed reaction vessel equipped with a stirrer were continuously fed a solution of ethylene in n-hexane and a solution of butene-1 in n-hexane at a total n-hexane feed rate of 80 kg/hr with the feed rates of ethylene and 1-butene being changed as shown in Table 1. Each of vanadyl trichloride, ethylaluminum sesquichloride, and n-butyl perchlorocrotonate was continuously fed to the vessel through the respective line at the respective feed rates as shown in Table 1. The inner temperature of the reaction vessel was controlled at 40° C. or 50° C. by circulating cooling water through the jacket. During the polymerization, the polymerization liquid was continuously withdrawn from the upper part of the vessel so as to maintain the vessel always in a state filled with the liquid to the limit. The polymerization reaction was ceased by addition of a small amount of methanol. After removing any residual monomers from the reaction mixture and washing the mixture with water, the solvent was removed by stripping to collect a solid copolymer produced, which was then dried at 80° C. under reduced pressure to obtain an ethylene-1-butene copolymer. The thus obtained copolymers were designated as I-A to I-E.

The polymerization conditions, the production rate of the copolymer, the density and MFR of the resulting copolymer, and the endothermic peak temperature (DSC melting point) in the DSC thermogram of the copolymer as determined after complete fusion and gradual cooling are shown in Table 1.

(2) Mixing of Copolymer (I) and High-Density Polyethylene

Each of Copolymers I-A to I-E as obtained in (1) above was blended with Nissan Polyethylene ® 1010 (hereinafter referred to as II-A), 2010 (hereinafter referred to as II-B) or 1070 (hereinafter referred to as II-C) at a mixing ratio shown in Table 3 or 4 by means of an intensive mixer, #0 Model manufactured by Nippon Roll Seizo K.K., at a revolution of 35 rpm and at a temperature of 150° C. for 10 minutes. At the time of blending, 0.20 part of calcium stearate, 0.15 part of Irganox ® 1076, 0.10 part of Sandostab ®P-EPQ, 0.08 part of erucamide, and 0.10 part (Examples 1 to 3 and Comparative Examples 1 and 2) or 0.40 part (Examples 4 to 11 and Comparative Examples 5 and 7) of a silica type anti-block agent were added to the mixture, each per 100 parts of the total resin content.

The Nissan Polyethylene ® series used as high-density polyethylene are ethylene-1-butene copolymers as proved by infrared analysis. The density and MFR of these polyethylene resins and the temperature at the endothermic peak in the DSC thermogram of each polyethylene resin as determined after complete fusion and gradual cooling and the half width of said peak are shown in Table 2.

Table 3 and 4 each shows the density and MFR of the resulting uniform mixture and the endothermic peak temperature, the ΔHb/ΔHa ratio, the (ΔHa+ΔHb)/ΔHt ratio, and the half width Wa_{178} in the DSC thermogram of the mixture as determined after complete fusion and gradual cooling.

(3) Production of Film

(i) Inflation (Examples 1 to 10 and Comparative Examples 1, 2, 5 and 7)

A 30 μm thick film was produced from each of the uniform polyethylene mixtures as prepared in (2) above by using an inflation molding machine, K-40R manufactured by Placo Corporation, equipped with a spiral die having a die diameter of 125 mm and a die lip of 2.0 mm and a single-stage air ring having an iris at a rate of extrusion of 24 kg/hr, at a die temperature of 170° C., and at a blow-up ratio of 1.8. Physical properties of each of the resulting films are shown in Tables 3 and 4. The films to be used in composite films are hereinafter described were subjected to corona discharge treatment with a corona discharge treating device so as to give a surface tension of from 42 to 45 dyne/cm.

(ii) T-Die Extrusion (Example 11)

A 30 μm thick film was obtained from each of the uniform polyethylene mixtures as prepared in (2) above by the use of a T-die film molding machine manufactured by Tanabe Plastic K.K. equipped with an extruder having an inner diameter of 50 mm, a T-die having a die width of 400 mm and a gap of 0.7 mm and a semi-matte roll at a resin temperature of 270° C., at a rate of extrusion of 6.4 kg/hr, and at a chill roll temperature of 75° C. the film was subjected to corona discharge treatment by means of a corona discharge treating device so as to give a surface tension of from 42 to 45 dyne/cm. Physical properties of each of the resulting films are shown in Table 4.

(4) Production of Composite Film

(i) Sandwich Lamination (Examples 1 to 3 and Comparative Examples 1 and 2)

A stretched nylon (thickness: 15 μm)/LDPE (thickness: 20 μm) base film and the film obtained in (3) above were laminated while extruding Sumikathene ® L705 having a resin temperature of 320° C. therebetween by the use of an extruder (diameter: 65 mm) manufactured by Sumitomo Chip Building and Machinary Co., Ltd. and a laminator, Model 550 manufactured by Tanabe Plastic Kikai K.K., to obtain a composite film having a sandwich structure whose intermediate layer had a thickness of 30 μm. The heat-sealing properties and hot tack of the resulting composite film are shown in Tables 5 and 6, respectively.

(ii) Dry Lamination (Examples 4 and 11 and Comparative Examples 5 and 7)

The film obtained in (3) above was press bonded on a 15 μm thick stretched nylon base film on which a urethane adhesive had been applied to a dry spread of 2 g/m² at a temperature of 40° C. and at a pressure of 3 kg/cm² by means of a bench test roller manufactured by Yasui Seiki K.K., and aged under heating at 40° C. for 2 days to obtain a dry lamination composite film. The heat-sealing properties and hot tack of the resulting composite film are shown in Tables 7 and 8, respectively.

COMPARATIVE EXAMPLE 3

A blown film and a composite film were produced in the same manner as in Example 2-(3) and (4), except for replacing the uniform polyethylene mixture as used in Example 2 with polyethylene of a Sumikathene ®-L series experimentally prepared by Sumitomo Chemical Co., Ltd. having a density of 0.913 g/cm³ and an MFR of 1.9 (identified as an ethylene-1-butene copolymer by infrared analysis). The DSC thermogram of this copolymer as determined after complete fusion and gradual cooling showed endothermic peaks at 103.0° C. and 120.4° C. and a minimum at 112.0° C. between these endothermic peaks. The ratio of the endotherm in the higher temperature side to the endotherm in the lower temperature side divided on the boundary at 112.0° C. was found to be 0.42, and the half width of the peak in the lower temperature side was found to be 34.2° C. The thermogram obtained by directly heating the film obtained from the copolymer showed a single peak at 116.0° C., with its half width being 29.8° C.

The properties of the resulting film and composite film are shown in Tables 3, 5 and 6.

EXAMPLE 4

A blown film and a composite film were produced in the same manner as in Example 2-(3) and (4), except for replacing the uniform polyethylene mixture as used in Example 2 with Ultzex ® 1520L produced by Mitsui Petrochemical Industries, Ltd. (density: 0.913 g/cm³; MFR: 2.5; identified as an ethylene-4-methyl-1-pentene copolymer having a 4-methyl-1-pentene content of 9.1% by infrared absorption analysis). In this case, since the copolymer pellets were found to contain 0.15 part of an anti-block agent per 100 parts of the copolymer, no anti-block agent was externally added. The DSC thermogram of the copolymer as determined after complete fusion and gradual cooling showed endothermic peaks at 102.3° C. and 119.3° C. and a minimum at 115.4° C. between these endothermic peaks. The ratio of the endotherm in the higher temperature side to the endotherm in the lower temperature side divided on the boundary at 115.4° C. was found to be 0.19, and the half width of the peak in the lower temperature side was found to be 31.4° C. The thermogram obtained by directly heating the film obtained from the copolymer showed a broad distribution, revealing a single peak at 109.4° C., with its half width being 27.6° C.

The properties of the resulting film and composite film are shown in Tables 3, 5 and 6.

EXAMPLE 12

(1) Preparation of Polyethylene by Two-Stage Polymerization

In a 100 l-volume jacketed reactor equipped with a stirrer were charged 60 of n-hexane and 60 g of ethylaluminum sesquichloride. The inner temperature of the reactor was elevated to 40° C. by circulating warm water through the jacket. Then, 3.0 kg/cm² of ethylene was fed, and 4 mg of vanadium trichloride was added to the mixture to initiate polymerization. During the reaction, ethylene was fed so as to maintain the ethylene pressure at 2.6 kg/cm². Twenty minutes later, 8 kg of 1-butene and 2.5 kg/cm² of hydrogen were fed, and 40 g of n-butyl perchlorocrotonate was added to the mixture. Four 40 g portions of n-butyl perchlorocrotonate were added thereto at intervals of 20 minutes. During the reaction, ethylene was fed so as to maintain the total pressure in the reactor constant, and cooling water was circulated through the jacket so as to maintain the inner temperature at 40° C. After 2 hours from the polymerization initiation, the gas in the reactor was purged, and the reaction mixture was poured into a large quantity of methanol to obtain a precipitate. The precipitate was filtered, and the filter cake was dried to obtain a polyethylene polymer.

The density and MFR of the resulting polymer, and the results of the DSC thermographic analysis of the polymer are shown in Table 4.

(2) Compounding with Additives

The polyethylene as obtained in (1) above was kneaded in an intensive mixer, Model #0 manufactured by Nippon Roll Seizo K.K., at 35 rpm and at 150° C. for 10 minutes together with 0.20 part of calcium stearate, 0.15 part of Irganox ® 1076, 0.10 part of Sandostab ® P-EQ, 0.08 part of erucamide, and 0.40 part of a silica type anti-block agent, each per 100 parts of the polyethylene.

(3) Production of Film and Composite Film

A blown film and a composite film were produced in the same manner as in Example 10-(3) and (4), except for using the polyethylene pellets as obtained in (2) above.

The results of the DSC thermographic analysis of the resulting film are shown in Table 4. The physical properties of the resulting film and composite film are shown in Tables 4, 7, and 8.

COMPARATIVE EXAMPLE 6

The procedures of Example 9-(3) and (4) wee repeated, except for replacing the uniform mixture as used in Example 9 with a compounded resin obtained by melt-kneading a polyethylene of a Sumikathene ®-L series experimentally prepared by Sumitomo Chemical

Co., Ltd. (density: 0.914 g/cm³; MFR: 2.7; identified as an ethylene-1-butene copolymer by infrared absorption analysis) and 0.40 part of a silica type anti-block agent per 100 parts of the copolymer.

The DSC thermogram of the above-described copolymer as determined after complete fusion and gradual cooling revealed endothermic peaks at 101.4° C. and 120.3° C. and the minimum at 111.8° C. between these endothermic peaks. The ratio of the endotherm in the lower temperature side to that in the higher temperature side on the boundary at this temperature of the minimum was 0.33, and the half width of the peak in the lower temperature side was 31.6° C. The DSC thermogram of the film showed a single peak at 109.5° C., the half width of which was 27.8° C.

The properties of the resulting film and composite film are shown in Tables 4, 7, and 8.

EXAMPLE 13 AND COMPARATIVE EXAMPLE 8

(1) Synthesis of Vanadium Catalyst (a)

In a 100 ml-volume flask whose atmosphere had been displaced with argon, 0.033 mol of vanadium trichloride and 26 ml of n-heptane were charged and heated to 60° C. To the mixture was added 0.165 mol of methyl alcohol, and the mixture was allowed to react at 50° C. for 1 hour while stirring in an argon stream. After the reaction, the supernatent liquor was withdrawn through a glass filter, and the solid was washed 3 times with 25 ml portions of n-heptane and dried under reduced pressure to obtain an n-heptane-insoluble vanadium compound as a dark green powder.

Compositional analysis by water-degradation revealed that the resulting vanadium compound comprised 21% of a vanadium atom, 42% of a chlorine atom, and 40% of CH_3OH. Accordingly, this compound was identified to be represented by formula $VCl_3.3.0CH_3OH$ (i.e., the compound of formula $V(OR)_mCl_{3-m}.nROH$, wherein m is 0, and n is 3.0). The powder X-ray diffraction spectrum of the compound showed no spectrum characteristic of vanadium trichloride.

(2) Preparation of Copolymer I-G

In a 100 l-volume jacketed reactor equipped with a stirrer were charged 60 l of n-hexane, 3.8 kg of 1-hexene, and 400 ml of a 10% hexane solution of ethylaluminum sesquichloride. The inner temperature of the reactor was elevated to 30° C. by circulating warm water through the jacket. Then, 1.5 kg/cm² of hydrogen and 4.5 kg/cm² of ethylene were fed, and to the mixture was added a mixture comprising 1.58 g of the vanadium catalyst (a) as obtained above and 70 ml of a 10% hexane solution of ethylaluminum sesquichloride to initiate polymerization. Five 1.25 ml portions of a 1 mmol/ml solution of n-butyl perchlorocrotonate at intervals of 20 minutes. During the reaction, ethylene was fed so as to maintain the total pressure in the reactor constant, and cooling water was circulated through the jacket so as to maintain the inner temperature at 30° C. After 2 hours from the polymerization initiation, the gas in the reactor was purged, and the reaction mixture was poured into a large quantity of methanol to obtain a precipitate. The precipitate was filtered, and the filter cake was dried to obtain an ethylene-1-hexene copolymer. The resulting copolymer was designated as I-G.

The density and MFR of the copolymer I-G and the results of the DSC thermographic analysis of I-G are shown in Table 4.

(3) Mixing of Copolymer (I) and High-Density Polyethylene:

Copolymer I-G as obtained in (2) above was mixed with Nissan Polyethylene ® 1010 (II-A) under the same conditions as in Example 9-(2). The MFR of the resulting mixture and the results of the DSC thermogram of the mixture as determined after complete fusion and gradual cooling are shown in Table 4.

(4) Production of Film and Composite Film

A film and a composite film were produced from the polyethylene pellets as obtained in (3) above in the same manner as in Example 10-(3) and (4)

The results of the DSC thermographic analysis of the film are shown in Table 4. The physical properties of the film and composite film are shown in Tables 4, 7, and 8.

COMPARATIVE EXAMPLE 9

The procedure of Example 13-(4) was repeated, except for replacing the uniform mixture as used in Example 13 with a compounded resin obtained by melt-kneading polyethylene of a Sumikathene ® α series experimentally prepared by Sumitomo Chemical Co., Ltd. (density: 0.913 g/cm³; MFR: 2.0; identified as an ethylene-1-hexene copolymer by infrared absorption analysis) and 0.40 part of a silica type anti-block agent per 100 parts of the copolymer.

The DSC thermogram of the above-described copolymer as determined after complete fusion and gradual cooling revealed endothermic peaks at 103.6° C. and 121.0° C. and the minimum at 114.0° C. between these endothermic peaks. The ratio of the endotherm in the lower temperature side to that in the higher temperature side on the boundary at this temperature of the minimum was 0.30, and the half width of the peak in the lower temperature side was 33.4° C. The DSC thermogram of the film showed a single peak at 109.4° C., the half width of which was 29.2° C.

The properties of the resulting film and composite film are shown in Tables 4, 7, and 8.

REFERENCE EXAMPLE

In order to examine the influence of a rate of temperature reduction preceding determination of DSC thermograms, A programed-temperature thermogram was determined for each of the uniform mixtures of Examples 1 to 3 and Ultzex ® 1520L used in Comparative Example 4 in the same manner as described above, except that the rate of temperature reduction preceding the determination was set at 10° C./min. The peak temperatures of the endothermic peaks of each thermogram are shown in Table 9. The peak temperatures of the thermograms of the same mixtures and Ultzex ® 1520L as determined in the foregoing examples (temperature reduction rate: 1° C/min) are also shown in Table 9. The thermograms of Example 2 and Comparative Example 4 are shown in FIGS. 1 and 2, respectively, in which the temperature reduction rate was 1° C./min, and in FIGS. 3 and 4, respectively, in which the temperature reduction rate was 10° C./min. On comparing FIGS. 1 and 2 with FIGS. 3 and 4, it can be seen that the peak in the higher temperature region, which is single-headed when the temperature reduction rate is 1°

C./min, is split up in some cases when the temperature is reduced at rate of 10° C./min. This splitting of peak seems to be because the lamellar crystals which have not been allowed to sufficiently grow under such rapid cooling undergo fusion-recrystallization in the subsequent temperature rise.

The DSC programed-temperature thermograms of the films obtained in Example 2 and Comparative Example 4 are shown in FIGS. 5 and 6, respectively. As is shown, the film of Example 2 shows clear peaks at 92.2° C. and 125.8° C., whereas the film of Comparative Example 4 shows a broad fusion pattern having a peak at 109.0° C.

TABLE 1

	Copolymer				
	I-A	I-B	I-C	I-D	I-E
Feed Rate:					
Ethylene (kg/hr)	1.4	3.4	3.7	3.5	3.2
1-Butene (kg/hr)	0.6	4.5	4.4	3.1	7.0
Vanadyl Trichloride (g/hr)	0.002	0.2	0.6	0.07	0.2
Ethylaluminum Sesquichloride (g/hr)	1.2	1.1	3.0	1.5	1.8
n-Butyl Perchloro-crotonate (g/hr)	0.72	4.6	—	0.4	0.9
Reaction Temperature (°C.)	40	50	50	50	50
Copolymer Production Rate (kg/hr)	1.4	2.7	2.0	1.8	2.4
Copolymer Produced:					
Density (g/cm³)	0.906	0.897	0.910	0.909	0.888
MFR (g/10 min)	2.1	1.7	1.9	1.7	1.7
DSC Melting point (1C)	92.9	79.8	97.3	96.5	65.4
DSC Half Width (1C)	19.5	22.3	16.8	15.4	21.6

TABLE 2

	High-Density PE (II)		
	II-A	II-B	II-C
Name (Nissan Polyethylene ®)	1010	2010	1070
MFR (g/10 min)	1.0	1.0	8.1
Density (g/cm³)	0.950	0.955	0.951
DSC Melting Point (°C.)	133.2	134.6	131.7
DSC Half Width (°C.)	5.6	6.0	5.0

TABLE 3

	Comparative Example 1	Example 1	Example 2	Example 3	Comparative Example 2	Comparative Example 3	Comparative Example 4
Polyethylene Mixture:							
Copolymer [I] (PHR)	I-A (100)	I-A (95)	I-A (85)	I-A (70)	I-A (30)	Sumikathene ® L (100)	Ultzex ® 1520 L (100)
HDPE (II) (PHR)	II-A (5)	II-A (15)	II-A (30)	II-A (70)			
Density (g/cm³)	0.905	0.908	0.913	0.920	0.913	0.913	0.913
MFR (g/10 min)	2.1	2.1	1.9	1.7	1.9	1.9	2.5
DSC Analysis:							
Melting Peak (°C.)	92.9	92.8	92.8	92.6	94.1	103.0	102.3
		124.3	125.7	128.6	132.1	120.4	119.3
ΔHb/ΔHa	—	0.16	0.52	1.2	5.19	0.42	0.19
(ΔHa + ΔHb)/ΔHt	—	1.0	1.0	1.0	1.0	1.0	1.0
Wsj (°C.)	—	19.4	19.9	21.3	27.4	34.2	31.0
Molding Process	inflation	inflation	inflation	inflation	inflation	inflation	inflation
DSC Analysis of Film:							
Melting Peak (°C.)	95.5	93.3	92.3	93.0	127.0	116.0	109.4
		105.9	113.0	117.9			
		124.2	125.7	126.4			
ΔHb/ΔHa	—	0.16	0.58	0.99	—	—	—
(ΔHa + ΔHb)/ΔHt	—	0.84	0.87	0.78	—	—	—
Wsj(°C.)	—	15.0	17.2	22.8	—	—	—
Film Properties:							
Haze (%)	2.5	3.0	6.1	9.9	14	13	9.8
Gloss (%)	147	144	122	101	85	70	103
1% Secant Modulus (kg/cm):							
MD	730	870	1180	1750	3760	900	1100
CD	770	950	1410	2250	5040	1200	1400
Dart Drop Impact Strength (kg · cm/mm)	2310	680	420	260	58	240	780
Elmendorf Tear Strength (kg/cm):							
MD	32	37	42	42	8	17	41
CD	63	75	109	158	265	190	154

TABLE 4

	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11
Polyethylene Mixture:								
Copolymer [I] (PHR)	I-B (85)	I-C (98)	I-C (94)	I-C (75)	I-C (95)	I-D (85)	I-D (85)	I-D (85)
HDPE (II) (PHR)	II-A (15)	II-A (92)	II-A (6)	II-A (25)	II-B (5)	II-A (15)	II-C (15)	II-A (15)
Density (g/cm³)	0.906	0.910	0.912	0.920	0.912	0.915	0.915	0.915
MFR (g/10 min)	1.7	1.7	1.9	1.9	1.9	1.6	2.0	1.5
DSC Analysis:								
Melting Peak (°C.)	79.7	91.2	97.1	96.6	97.0	97.1	96.8	97.1
	125.7	120.3	122.8	126.7	124.9	124.9	124.8	124.9
ΔHb/ΔHa	0.79	0.10	0.21	0.42	0.19	0.36	0.36	0.36
(ΔHa + ΔHb)/ΔHt	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

TABLE 4-continued

W_{4j} (°C.)	21.8	17.2	17.2	19.3	14.0	17.0	17.4	17.0
Molding Process	inflation	inflation	inflation	inflation	inflation	inflation	inflation	inflation
DSC Analysis of Film:								
Melting Peak (°C.)	81.4	98.1	95.9	96.0	96.5	96.3	96.3	95.2
	112.2		106.9	116.8	109.0	112.4	111.1	109.9
	125.7	122.4	123.7	125.9	126.1	125.2	124.2	125.3
ΔHb/ΔHa	1.02	0.05	0.23	0.93	0.22	0.53	0.46	0.63
(ΔHa + ΔHb)/ΔHt	0.91	1.0	0.78	0.84	0.81	0.84	0.80	0.78
W_{4j} (°C.)	17.9	18.9	17.2	22.7	14.8	16.9	17.0	20.8
Film Properties:								
Haze (%)	7.0	6.3	6.7	12	11	7.9	7.9	3.7
Gloss (%)	107	119	116	97	89	99	103	142
1% Secant Modulus (kg/cm):								
MD	960	950	1060	1740	1140	1380	1360	1100
CD	1070	980	1130	2160	1280	1600	1630	1110
Dart Drop Impact Strength (kg · cm/mm)	2800<	680	510	270	560	630	580	620
Elmendorf Tear Strength (kg/cm):								
MD	52	29	31	33	33	36	36	30
CD	84	71	83	145	82	83	70	125

	Example 12	Comparative Example 5	Comparative Example 6	Comparative Example 7	Example 13	Comparative Example 8	Comparative Example 9
Polyethylene Mixture:							
Copolymer [I] (PHR)	Two-stage polymer (100)	I-E (70)	Sumikathene ® L (100)	I-D (100)	I-G (85)	I-G (100)	Sumikathene ® α (100)
HDPE (II) (PHR)		II-A (30)			II-A (15)		
Density (g/cm³)	0.912	0.907	0.914	0.90	0.912	0.906	0.913
MFR (g/10 min)	1.8	1.5	2.7	1.7	1.8	1.8	2.0
DSC Analysis:							
Melting Peak (°C.)	94.8	67.4	101.4	96.5	93.5	93.8	103.6
	126.5	127.7	120.3		125.2		121.0
ΔHb/ΔHa	0.14	4.64	0.33	—	0.51	—	0.30
(ΔHa + ΔHb)/ΔHt	1.0	1.0	1.0	—	1.0	—	1.0
W_{4j} (°C.)	13.1	22.3	31.6	—	19.7	—	31.4
Molding Process	inflation	inflation	inflation	inflation	inflation	inflation	inflation
DSC Analysis of Film:							
Melting Peak (°C.)	93.8	67.4	100.3	98.0	93.0	96.6	109.2
	107.3	117.7			111.9		
	126.0	126.9			125.1		
ΔHb/ΔHa	0.10	7.04	—	—	0.60	—	—
(ΔHa + ΔHb)/ΔHt	0.88	0.82	—	—	0.89	—	—
W_{4j} (°C.)	16.0	17.7	—	—	19.3	—	—
Film Properties:							
Haze (%)	6.2	10.2	30	4.7	8.6	5.3	27.4
Gloss (%)	121	93	41	129	97	125	40
1% Secant Modulus (kg/cm):							
MD	940	1250	1170	860	1240	710	1090
CD	990	1500	1310	930	1450	780	1260
Dart Drop Impact Strength (kg · cm/mm)	640	630	220	2900	2900<	2900<	900
Elmendorf Tear Strength (kg/cm):							
MD	30	82	34	31	91	73	101
CD	85	125	119	53	164	107	183

TABLE 5

	Peel Strength of Heat-Sealed Area (kg/15 mm; 180° C.)						
Heat-Sealing Temperature (°C.)	Comparative Example 1	Example 1	Example 2	Example 3	Comparative Example 2	Comparative Example 3	Comparative Example 4
85	0.00	0.00	0.00	0.00			
90	0.01	0.03	0.03	0.01			0.00
95	0.02	0.15	0.07	0.04			0.03
100	0.04	0.81	1.33	0.17		0.00	0.06
105	0.24	2.91	3.80	0.67	0.00	0.01	0.69
110	0.53	4.00	4.79	3.30	0.03	0.10	1.96
115	1.21	5.39	5.36	3.88	0.04	0.30	3.10
120	2.81	5.51	6.36	4.03	0.08	2.15	3.88
125	3.83	5.42	6.01	5.33	0.15	4.50	5.36
130	5.55	5.94	5.79	6.00	0.21	4.95	5.38
135	5.34	6.22	6.19	5.85	0.47	5.50	6.58
140	4.78	6.20	6.44	5.27	1.48	5.90	4.94
145					4.67		

TABLE 5-continued

Heat-Sealing Temperature (°C.)	Comparative Example 1	Example 1	Example 2	Example 3	Comparative Example 2	Comparative Example 3	Comparative Example 4
	Peel Strength of Heat-Sealed Area (kg/15 mm; 180° C.)						
150					4.50		

TABLE 6

Heat-Sealing Temperature (°C.)	Comparative Example 1	Example 1	Example 2	Example 3	Comparative Example 2	Comparative Example 3	Comparative Example 4
	Peel Length (mm) of Heat-Sealed Area While Hot						
100		20<	20<				
105		17.0	18.3				
110	13.7	14.0	20<				
115		10.5	10.9	14.2		20<	20<
120	20<	4.3	6.3	12.5		18.2	14.7
125	15.2	1>	1>	8.6		16.5	13.0
130	9.2	1>	1>	8.2		13.0	7.5
135	4.4	1>	1>	6.2		3.4	1<
140	1>	1>	1>	3.0		1.2	1<
145	cut*	2.7	1>	4.9		4.0	1<
150		cut	1.5	1.8	20<	cut	1<
155			cut	cut	16.1		cut
160					7.9		
165					4.7		
170					cut		

Note:
*The sealant layer was cut off.

TABLE 7

Heat-Sealing Temp. (°C.)	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Ex. 13	Comp. Ex. 8	Comp. Ex. 9
	Peel Strength of Heat-Sealed Area (kg/15 mm; 180° C.)														
70	0.03									0.03			0		
75	0.07					0				1.70			0.01	0	
80	2.03					0.03				3.28			0.02	0.01	0
85	2.95	0	0	0	0	0.73	0	0	0	4.17	0	0.03	0.01	0.01	
90	3.42	0.07	0.17	0.03	0.06	1.13	0.01	0.01	0.10	5.35	0.01	0.02	0.16	0.23	0.02
95	3.80	0.83	0.93	0.09	1.35	1.47	0.21	0.04	1.00	4.83	0.02	0.15	1.10	0.47	0.05
100	3.76	2.09	2.19	0.76	2.71	3.28	1.45	1.23	2.51	4.94	0.04	2.15	1.82	1.58	0.33
105	4.23	3.43	4.00	3.20	4.56	3.83	1.45	2.02	4.22	4.80	0.42	3.03	2.28	2.47	1.87
110	4.25	3.81	4.45	3.12	5.39	4.23	1.88	2.15	5.12	5.03	1.83	4.05	3.12	3.30	2.32
115	4.42	4.26	4.30	3.56	5.65	4.80	2.42	3.20	5.60	5.12	2.06	4.58	3.25	3.85	3.92
120	4.57	4.45	3.59	3.62	5.74	5.13	2.97	3.38	5.70	5.63	3.85	4.93	3.65	4.13	4.32
125	4.88			4.17	5.33	5.47	3.30	3.95	5.66	5.48	4.78	4.90	4.20	4.20	4.70
130	4.95			4.63		5.67	4.20	4.80	5.35	5.38	5.17	5.00	4.75	4.42	5.57
135	5.00					5.88	4.95	5.72	5.80	6.03		4.93	5.18	4.83	5.65
140	5.22					5.75	5.32	5.77	5.12	5.88	5.33	4.87	5.27	4.98	5.75

TABLE 8

Heat-Sealing Temp. (°C.)	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Ex. 13	Comp. Ex. 8	Comp. Ex. 9
	Peel Length (mm) of Heat-Sealed Area While Hot														
80	20<									13.9					
85	12.5									10.2					
90	8.0									7.1					
95	6.0					20<				9.1			20<	20<	
100	7.8	20<	20<	20<	20<	18.6	20<	20<	20<	8.2		20<	13.0	13.8	
105	3.3	13.3	11.0	17.6	18.1	6.0	15.5	16.5	16.1	9.9		15.4	10.0	10.2	20<
110	5.2	12.7	7.2	15.0	6.9	1.4	11.5	11.4	7.0	10.9	20<	5.1	4.0	6.8	14.8
115	6.9	4.7	2.7	11.5	2.5	1.5	10.5	8.8	3.1	12.3	13.5	2.9	5.2	4.5	11.0
120	7.5	2.3	2.6	6.8	2.6	1.5	5.4	4.7	2.3	14.4	8.2	2.1	1.2	1.5	6.0
125	8.1	2.6	2.5	5.7	2.9	3.9	6.1	3.7	2.1	12.7	4.3	2.9	0.5	0.8	2.5
130	8.8	3.0	2.6	4.6	4.0	4.3	3.6	2.3	2.5	14.6	2.2	3.0	0.5	2.0	1.5
135	6.9	4.5	3.9	4.3	5.1	4.1	4.1	3.7	2.2	16.7	2.7	5.2	0.5	1.5	0.5
140	10.1	4.9	4.9	3.8	4.8	4.7	5.8	4.8	3.3	14.8	3.8	7.1	1.3	3.0	0.5
145	11.9	6.7	7.4	5.4	8.5	5.5	9.9	5.4	5.0	9.9	5.8	11.0	1.8	4.0	1.0
150	14.2	8.6	8.4	7.7		10.3	13.3	7.9	8.4	10.3	8.0	15.5	2.7	6.0	2.0

TABLE 9

Example No.	Endothermic Peak Temperature (°C.) Rate of Temperature Reduction 1° C./min			10° C./min	
Example 1	92.8	124.3	93.6	(121.0)	124.8
Example 2	92.8	125.7	92.3	123.6	(126.5)*
Example 3	92.6	128.6	91.9	126.1	
Comparative Example 4	102.3	119.3	102.6	116.0	(119.8)*

Note:
*The parentheses indicate that the peak looks like a peak due to a peak-height change of less than 1/10 the maximum peak-height.

Making comparisons between Example 2 and Comparative Examples 3 and 4 in Tables 5 and 6, between Examples 5 to 10 and 12 and Comparative Example 6 in Tables 7 and 8, and between Example 13 and Comparative Example 9 in Tables 7 and 8, it can be seen that the films according to the present invention begin to exhibit heat-sealing properties and hot tack at lower temperatures and also the temperature range in which hot tack can be exhibited is markedly broader as compared with the comparative films. It can further be seen from Table 8 that the composite film of Comparative Example 5, in which the density of the polyethylene mixture is substantially equal to those of the polyethylene mixtures of Examples 4 and 5, shows a longer minimum peel length, i.e., lower strength, than Examples 4 and 5. Furthermore, making comparisons between the Examples and Comparative Examples with densities being equal. The films of the Examples are incomparably superior to the films obtained from the conventional L-LDPE in transparency (haze), gloss, and impact strength as well as nerve (expressed in terms of secant modulus at 1% strain).

Thus, the films according to the present invention are decidedly excellent as packaging film as compared with the conventional films.

As discussed above, the present invention provides low-density polyethylene films which highly satisfy all the physical properties required for use as packaging film, i.e., heat-sealing properties, hot tack, transparency, gloss, nerve, impact strength, and tear strength, and are therefore suitable as packaging film. The present invention also provides materials for providing such excellent films.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. An ethylene-α-olefin copolymer comprising ethylene and an α-olefin having from 4 to 10 carbon atoms, the copolymer having an α-olefin content of from 1.0 to 8.0 mol %, a density of from 0.900 to 0.930 g/cm³, and a melt flow rate of from 0.1 to 100 g/10 min., the programed-temperature thermogram of said copolymer as determined with a differential scanning calorimeter after being completely melted and then gradually cooled showing an endothermic peak (a) in a range of from 75° to 100° C. and an endothermic peak (b) in a range of from 120° to 140° C., with the ratio of an endotherm at the endothermic peak (b), αHb, to an endotherm at the endothermic peak (a), αHa, being from 0.03 to 2.0.

2. A film comprising an ethylene-α-olefin copolymer comprising ethylene and an α-olefin having from 4 to 10 carbon atoms, the copolymer having an αolefin content of from 1.0 to 8.0 mol %, a density of from 0.900 to 0.930 g/cm³, and a melt flow rate of from 0.1 to 100 g/10 min., the programed-temperature thermogram of said copolymer as determined with a differential scanning calorimeter after being completely melted and then gradually cooled showing an endothermic peak (a) in a range of from 75° to 100° C. and an endothermic peak (b) in a range of from 120° to 140° C., with the ratio of an endotherm at the endothermic peak (b), ΔHb, to an endotherm at the endothermic peak (a), ΔHa, being from 0.03 to 2.0.

3. A composite film composed of a base having provided on at least one surface thereof a film comprising an ethylene-α-olefin copolymer comprising ethylene and an α-olefin having from 4 to 10 carbon atoms, the copolymer having an α-olefin content of from 1.0 to 8.0 mol %, a density of from 0.900 to 0.930 g/cm³, and a melt flow rate of from 0.1 to 100 g/10 min., the programed-temperature thermogram of said copolymer as determined with a differential scanning calorimeter after being completely melted and then gradually cooled showing an endothermic peak (a) in a range of from 75° to 100° C. and an endothermic peak (b) in a range of from 120° to 140° C., with the ratio of an endotherm at the endothermic peak (b), ΔHb, to an endotherm at the endothermic peak (a), ΔHa, being from 0.03 to 2.0.

4. A low-density polyethylene film whose programed-temperature thermogram as determined directly for the film state with a differential scanning calorimeter shows an endothermic peak (a) in a range of from 75° to 100° C. and an endothermic peak (b) in a range of from 120° to 140° C., with the ratio of an endotherm at the endothermic peak (b), ΔHb, to an endotherm at the endothermic peak (a), ΔHa, being from 0.03 to 2.0.

5. A composite film composed of a base having provided on at least one surface thereof a low-density polyethylene film whose programed-temperature thermogram as determined directly for the film state with a differential scanning calorimeter shows an endothermic peak (a) in a range of from 75° to 100° C. and an endothermic peak (b) in a range of from 120° to 140° C., with the ratio of an endotherm at the endothermic peak (b), ΔHb, to an endotherm at the endothermic peak (a), ΔHa, being from 0.03 to 2.0.

6. A polyethylene mixture having a density of from 0.900 to 0.930 g/cm³ and a melt flow rate of from 0.1 to 100 g/10 min., which comprises (I) from 60 to 99 parts by weight of an ethylene-α-olefin random copolymer comprising ethylene and an α-olefin having from 4 to 10 carbon atoms, the copolymer having an α-olefin content of from 2.0 to 10 mol % and a density of from 0.895 to 0.915 g/cm³, the programed-temperature thermogram of said copolymer as determined with a differential scanning calorimeter after being completely melted and then gradually cooled showing an endothermic peak in a range of from 75° to 100° C., with the ratio of an endotherm at said peak to the total endotherm being at least 0.8, and (II) from 1 to 40 parts by weight of a high-density polyethylene having a density of at least 0.945 g/cm³, the programed-temperature thermogram of said high-density polyethylene as determined with a differential scanning calorimeter after being completely melted and allowed to cool showing an endothermic peak at 125° C. or higher, wherein the sum of (I) and (II) amounts to 100 parts by weight.

7. A film comprising a polyethylene mixture having a density of from 0.900 to 0.930 g/cm^3 and a melt flow rate of from 0.1 to 100 g/10 min., which comprises (I) from 60 to 99 parts by weight of an ethylene-α-olefin random copolymer comprising ethylene and an α-olefin having from 4 to 10 carbon atoms, the copolymer having an α-olefin content of from 2.0 to 10 mol % and a density of from 0.895 to 0.915 g/cm^3, the programed-temperature thermogram of said copolymer as determined with a differential scanning calorimeter after being completely melted and then gradually cooled showing an endothermic peak in a range of from 75° to 100° C., with the ratio of an endotherm at said peak to the total endotherm being at least 0.8, and (II) from 1 to 40 parts by weight of high-density polyethylene having a density of at least 0.945 g/cm^3, the programed-temperature thermogram of said high-density polyethylene as determined with a differential scanning calorimeter after being completely melted and allowed to cool showing an endothermic peak at 125° C. or higher, wherein the sum of (I) and (II) amounts to 100 parts by weight.

8. A composite film composed of a base having provided on at least one surface thereof a film comprising a polyethylene mixture having a density of from 0.900 to 0.930 g/cm^3 and a melt flow rate of from 0.1 to 100 g/10 min., which comprises (I) from 60 to 99 parts by weight of an ethylene-α-olefin random copolymer comprising ethylene and an α-olefin having from 4 to 10 carbon atoms, the copolymer having an α-olefin content of from 2.0 to 10 mol % and a density of from 0.895 to 0.915 g/cm^3, the programed-temperature thermogram of said copolymer as determined with a differential scanning calorimeter after being completely melted and then gradually cooled showing an endothermic peak in a range of from 75° to 100° C., with the ratio of an endotherm at said peak to the total endotherm being at least 0.8, and (II) from 1 to 40 parts by weight of a high-density polyethylene having a density of at least 0.945 g/cm^3, the programed-temperature thermogram of said high-density polyethylene as determined with a differential scanning calorimeter after being completely melted and allowed to cool showing an endothermic peak at 125° C. or higher, wherein the sum of (I) and (II) amounts to 100 parts by weight.

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