EXHIBIT V

PART 3

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/cm^3 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/cm^2, preferably from 0.88 to 0.90 g/cm^3, 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/cm^3) 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/cm^3, 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 drawing 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 Example 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 in 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 ($Wa_{\frac{1}{2}}$) of not more than 30° C., more preferably not more than 27° C., most preferably not more than 25° C. $Wa_{1/8}$ 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, $Wa_{1/8}$ is a temperature difference between the temperature at this intersection and the other intersection. If $Wa_{1/8}$ 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 in 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, antiblock 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 soupe; 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 $\Delta Hb/\Delta Ha$ ratio, the $(\Delta Ha+\Delta Hb)/\Delta Ht$ 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	136.6	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	92.8 124.3	92.8 125.7	92.6 128.6	94.1 132.1	103.0 120.4	102.3 119.3
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
$Wa_{\frac{1}{2}}$ (°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.)	96.5	93.3 105.9 124.2	92.3 113.0 125.7	93.0 117.9 126.4	127.0	116.0	109.4
ΔHb/ΔHa	—	0.16	0.58	0.99	—	—	—
(ΔHa + ΔHb)/ΔHt	—	0.84	0.87	0.78	—	—	—
$Wa_{\frac{1}{2}}$(°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	98	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.)	79.7 125.7	91.2 120.3	97.1 122.8	96.6 126.7	97.0 124.9	97.1 124.9	96.8 124.8	97.1 124.9
ΔHb/ΔHa	0.79	0.10	0.21	0.82	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_{81} (°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	93.9	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_{81} (°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	61.4	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_{81} (°C.)	13.1	22.3	31.6	—	19.7	—	33.4
Molding Process	inflation	inflation	inflation	inflation	inflation	inflation	inflation
DSC Analysis of Film:							
Melting Peak (°C.)	92.8	67.4	109.5	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_{81} (°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

Heat-Sealing Temperature (°C.)	Peel Strength of Heat-Sealed Area (kg/15 mm; 180° 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	2.08	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		5.87	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	3.7	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	1.4.4	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/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), 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/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, 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/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, 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/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.

7. A film comprising 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 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.

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/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.

* * * * *

United States Patent [19]
Fukushima et al.

[11] 4,438,238
[45] Mar. 20, 1984

[54] LOW DENSITY COPOLYMER COMPOSITION OF TWO ETHYLENE-α-OLEFIN COPOLYMERS

[75] Inventors: Nobuo Fukushima, Ootsu; Shuji Kitamura, Ibaraki; Kiyohiko Nakae, Nishinomiya; Tadatoshi Ogawa, Takatsuki; Kozo Kotani; Hidekazu Hosono, both of Toyonaka, all of Japan

[73] Assignee: Sumitomo Chemical Company, Limited, Osaka, Japan

[21] Appl. No.: 342,428

[22] Filed: Jan. 25, 1982

[30] Foreign Application Priority Data

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Jan. 30, 1981	[JP]	Japan	56-14039
Jan. 30, 1981	[JP]	Japan	56-14040
Jan. 30, 1981	[JP]	Japan	56-14041
Jan. 30, 1981	[JP]	Japan	56-14042
Jan. 30, 1981	[JP]	Japan	56-14043
Jan. 30, 1981	[JP]	Japan	56-14044

[51] Int. Cl.³ C08F 297/08; C08L 23/06; C08L 23/08

[52] U.S. Cl. ..... 525/240; 502/152; 264/176 R; 428/218; 428/220; 525/53; 525/247; 526/79; 526/346; 526/348.2; 526/348.4; 526/348.5; 526/348.6; 528/482

[58] Field of Search 525/240

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Primary Examiner—Stanford M. Levin
Attorney, Agent, or Firm—Stevens, Davis, Miller & Mosher

[57] ABSTRACT

An ethylene-α-olefin copolymer composition comprising two ethylene-α-olefin copolymers which are different in density, intrinsic viscosity and the number of short chain branching per 1000 carbon atoms. Extrusion processed materials, injection molded materials and films obtained from said composition are excellent in strength.

23 Claims, 9 Drawing Figures

research publications

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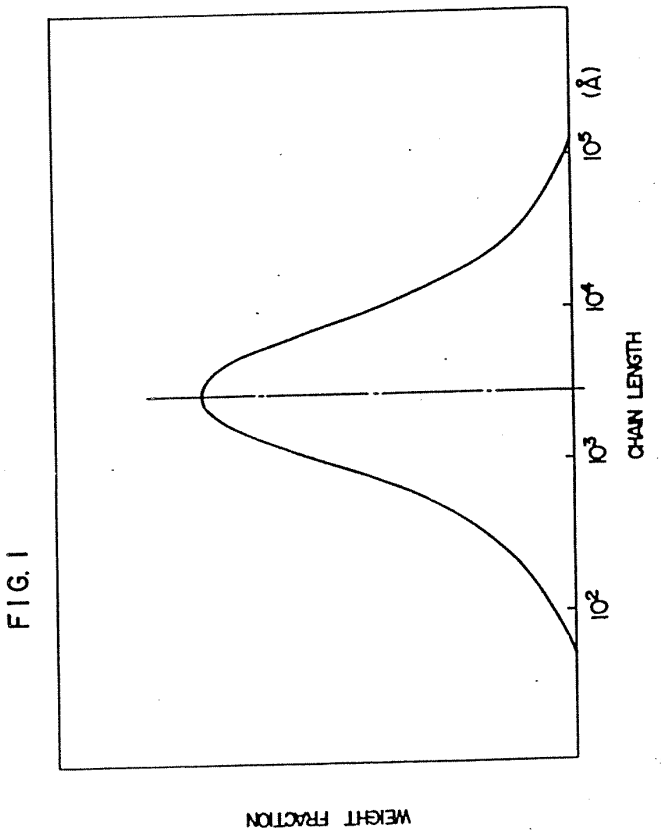


FIG. 1

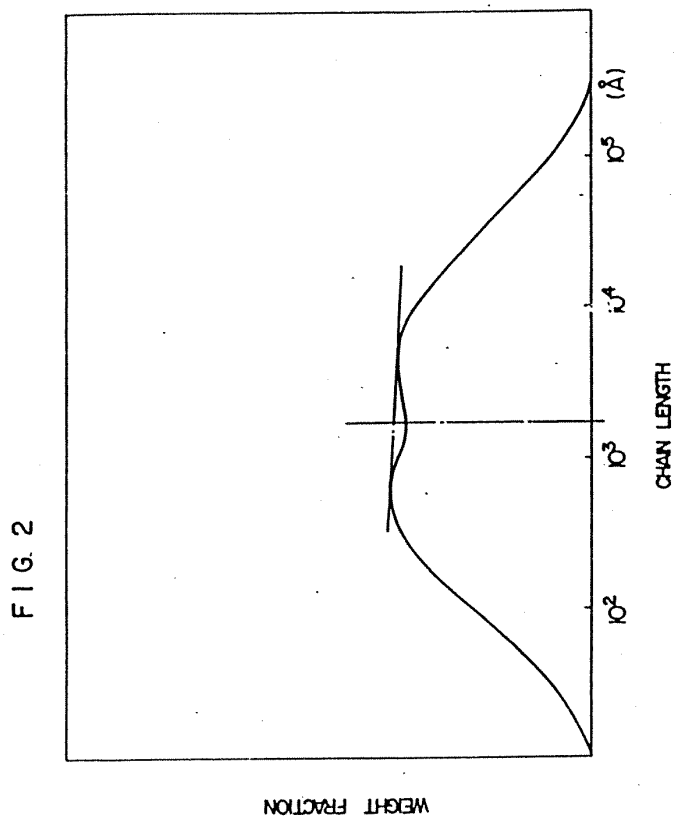


FIG. 2

research publications

4438238

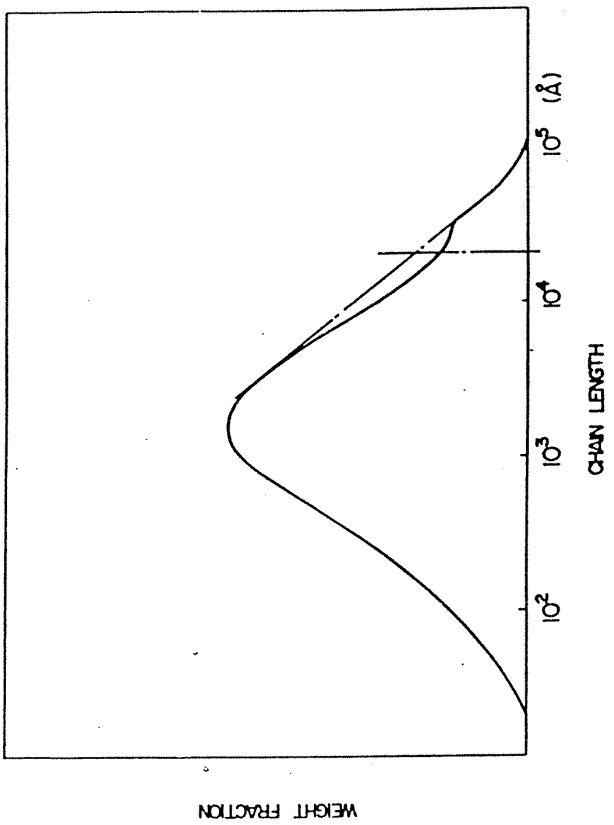


FIG. 3

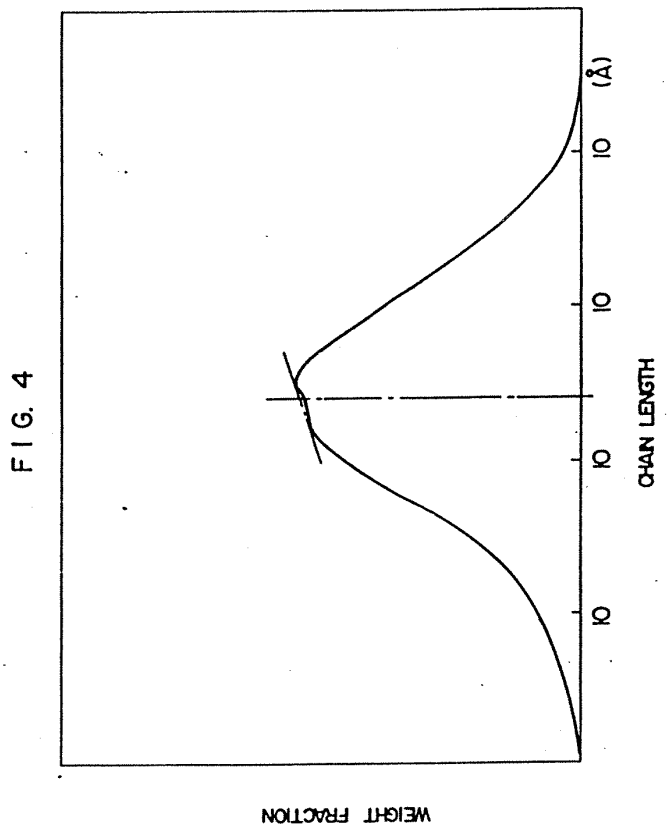


FIG. 4

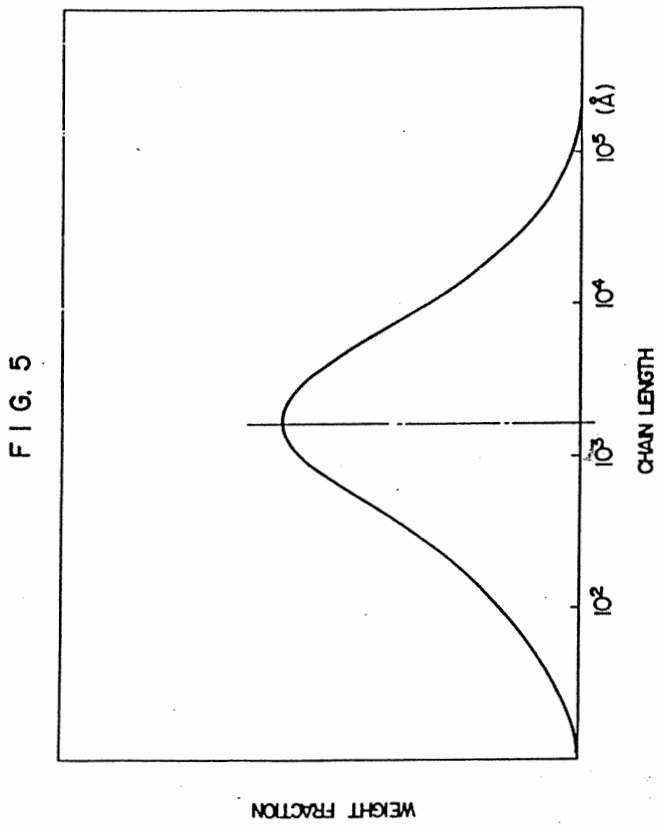


FIG. 5

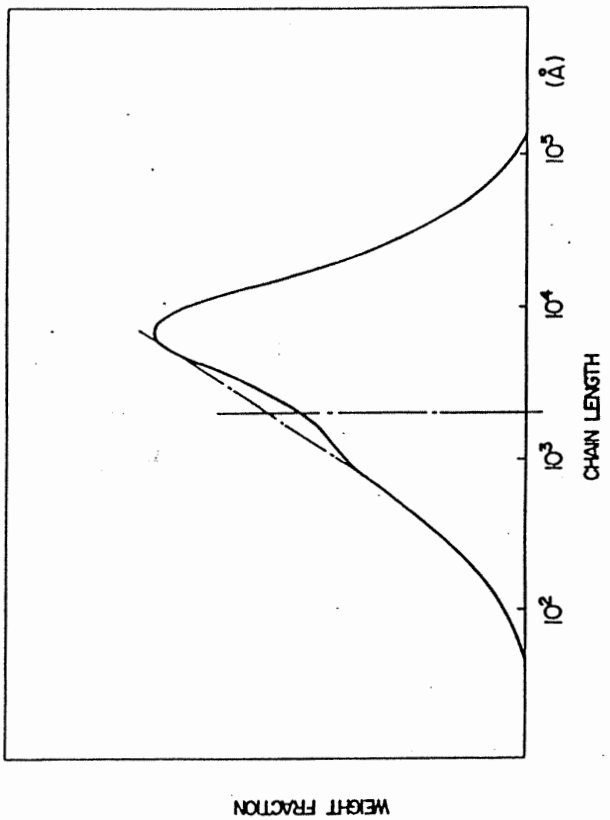


FIG. 6

FIG. 7

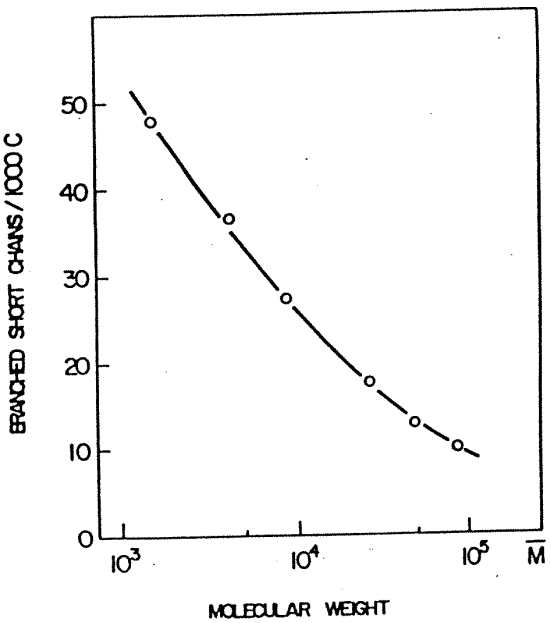

BRANCHED SHORT CHAINS / 1000 C
50
40
30
20
10
0
10^3
10^4
10^5
$\bar{M}$
MOLECULAR WEIGHT

FIG. 8

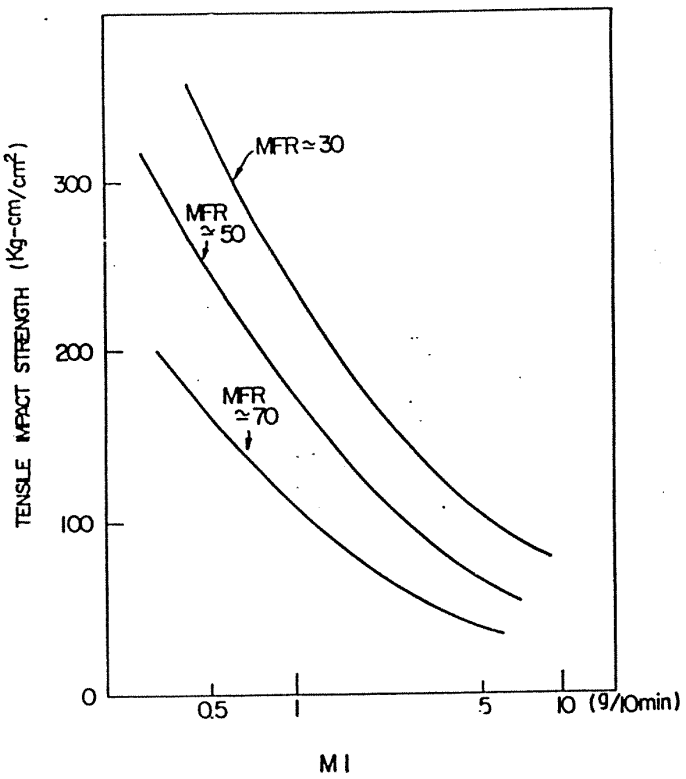
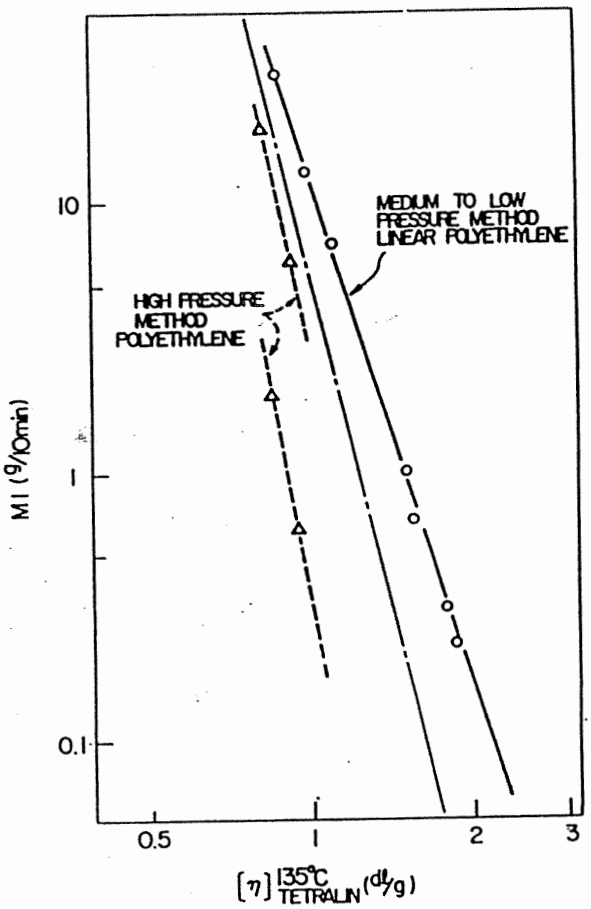

TENSILE IMPACT STRENGTH (Kg-cm/cm²)
300
200
100
0
MFR≃30
MFR ≃50
MFR ≃70
0.5
1
5
10 (g/10min)
MI

FIG. 9


MEDIUM TO LOW PRESSURE METHOD LINEAR POLYETHYLENE
HIGH PRESSURE METHOD POLYETHYLENE
MI (g/10min)
10
1
0.1
0.5
1
2
3
[η] 135°C TETRALIN (dl/g)

LOW DENSITY COPOLYMER COMPOSITION OF TWO ETHYLENE-α-OLEFIN COPOLYMERS

The present invention relates to an ethylene-α-olefin copolymer composition. More particularly, the present invention relates to ethylene-α-olefin copolymer compositions excellent in processability, impact strength, tensile strength, environmental stress cracking resistance, low temperature resistance, creep characteristics, tear strength, transparency, heat-sealing characteristics and chemical characteristics such as chemicals resistance, which is obtained by mixing an ethylene-α-olefin copolymer of a relatively higher molecular weight and an ethylene-α-olefin copolymer of a relatively lower molecular weight.

Being excellent in melt rheology characteristics as well as in physical and chemical properties, low density polyethylenes manufactured by the high pressure method (hereinafter referred to as "high pressure polyethylene") have been used for various uses such as films, sheets, pipes, blow bottles, injection molded products, coating materials for steel pipes and foam-molded materials. As mentioned above, high pressure polyethylenes are excellent in melt rheology characteristics, and therefore, they are excellent in processability. When used for extrusion processing or injection molding, their production efficiency is high, resulting in relatively low electricity consumption. In blown film processing, the above polyethylenes give good bubble stability. In cast film processing and extrusion lamination processing, there is only slight "neck-in". In blow molding, these polyethylenes give good parison stability. However, when they are processed into molded products, their mechanical strengths, such as tensile strength and impact strength, are relatively low and accordingly these products can not be used in thin forms.

High pressure polyethylenes have various other problems. They are used in many fields as films. Films of high pressure polyethylenes are required to have the following properties in recent, highly developed automatic packaging systems.

(1) Good heat-sealing property at low temperatures.

(2) High sealing strength in a condition where heat-sealed portions are not cooled sufficiently therefore not solidified yet (this strength is called "hot tack" strength). Hot tack strength is required because filling of contents and heat sealing are done almost at the same time.

(3) Sealing strength in a state where heat-sealing portions are contaminated with oils and the like, in packaging of oils and the like. (This strength is called heat sealing strength in contaminated condition.) However, high pressure polyethylenes are not satisfactory in hot tack and heat sealing strength in contaminated condition. When these polyethylenes are used in blow bottles, pipes and injection molded products, they are inadequate in environmental stress cracking resistance, therefore, cause occasional troubles and are susceptible to attack by chlorine water. Further, they are not sufficient in creep characteristics, which makes them unusable in pipes of high internal pressure. When high pressure polyethylenes are used as coating materials for steel pipes, their low temperature resistance is not satisfactory, which makes their use in very cold climatic areas improper. In their use as coating materials for electric wires, troubles occur at times due to improper

environmental stress cracking resistance and water-tree resistance.

To improve these defects, some attempts have been made. However, the quality is still not at a satisfactory level.

For improvement of these defects, the following polymerization methods have been adopted.

(1) Polymerization of ethylene and other polymerizable monomer such as vinyl acetate.

(2) Method in which ethylene and acrylic acid (or methacrylic acid) are polymerized followed by conversion to a salt with a metal, namely an ionomer.

The former method still has many problems such as (a) reduction of tear strength, rigidity and heat resistance of films, (b) occurrence of corrosion of extruder and smell in processing due to liberation of acetic acid and (c) occurrence of blocking due to sticky film surface and cold flow. The latter method has problems of reduction of thermal stability and weather resistance and of high cost.

Also for improvement of the defects of high pressure polyethylenes, there were made proposals in which a high pressure polyethylene is mixed with another α-olefin polymer such as high density polyethylene, polypropylene, polybutene, or a rubber. However, an improvement in one defect causes another problem and no satisfactory answer has been attained.

As resins which have low densities about equal to those of high pressure polyethylenes, there are known resins which are prepared by co-polymerizing ethylene and an α-olefin under a medium to low pressure using a transition metal catalyst. (Hereinafter, such are abbreviated as "ethylene-α-olefin copolymers".). The copolymers produced with a vanadium catalyst are low in degree of crystallization, and have problems in heat resistance, weather resistance and mechaical strengths. The ethylene-α-olefin copolymers produced under normal polymerization conditions with a titanium catalyst, having generally narrow molecular weight distributions (narrower than those of high pressure polyethylene.), are relatively excellent in mechanical strengths but poor in melt rheology characteristics and have many problems in processing. In blown film processing, a large quantity of electricity is needed, output is reduced or bubble stability is lost. In high speed processing, "shark skin" appears on film surfaces, thereby decreasing product values. Also in blow molding, parison stability is lost, or surfces of molded products turn to "shark skin" and product values are lost. In injection molding, processing temperatures need to be largely raised because of poorer flow property under high pressures as compared with high pressure polyethylenes, which requires more heat energy and moreover causes resin deterioration.

Trials have been made in recent years for solving these problems by improving extruders, screws and dies. These approaches require a large amount of expenditures and moreover techniques have not been fully developed. Further, various other problems such as the following have been encountered:

(1) with respect to mechanical strengths of films produced, balancing of machine direction (MD) and transverse direction (TD) is difficult and the tear strength of MD is poorer than that of high pressure polyethylenes, and

(2) film transparency is inferior to that of high pressure polyethylenes, because the ethylene-α-olefin copolymer of narrow molecular weight distribution has a

faster crystalization speed than high pressure polyethylenes and causes melt fractures more easily.

Low density ethylene-α-olefin copolymers are difficult to obtain under normal polymerization conditions using a chromium catalyst, because copolymerizability between ethylene and α-olefin is generally lower with chromium catalysts than with titanium catalysts. When a chromium-titanium catalyst is used in order to overcome this problem, ethylene-α-olefin copolymers obtained have wider molecular weight distributions than copolymers produced with a titanium catalyst and have slightly improved processability. However, their mechanical strengths largely worsen and their physical properties are not much different from those of high pressure polyethylenes and these copolymers provide film sheets and bottles inferior in transparency.

For attemping to improve the transparency of these copolymers, when the quantity of an α-olefin is largely increased in polymerization and the density of the copolymer obtained is reduced, only a sticky copolymer having much deteriorated mechanical strengths is produced.

According to the knowledge of the present inventors, ethylene-α-olefin copolymers polymerized under a medium to low pressure using a transition metal catalyst, have non-uniform component distributions. Namely in these copolymers, the number of short chain branching per 1000 carbon atoms (excluding methyl groups at the ends) (hereinafter referred to as "S.C.B." for brevity) varies depending upon molecular weight, and generally lower molecular weight components have larger S.C.B. and higher molecular weight components have smaller S.C.B. This phenomenon is considered to be due to that α-olefins tend to act as a chain transfer agent or act even to active sites of catalyst to which molecular weight regulators such as hydrogen tend to act. (cf. Reference example 1.)

Because of the above phenomenon, ethylene-α-olefin copolymers polymerized with the α-olefin concentration increased with an aim to reduce to a large extent the density of copolymers produced, only give such products as those having increased S.C.B. in their lower molecular weight components, thereby having increased solubility in solvents and poor mechanical strengths and causing surface stickiness. This tendency is particularly remarkable in those ethylene-α-olefin copolymers which are polymerized with a catalyst giving wider molecular weight distributions. One of the reasons for poor mechanical strengths of ethylene-α-olefin copolymers having wide molecular weight distributions will be explained by the above fact.

As described above, ethylene-α-olefin copolymers having densities about equal to those of high pressure polyethylenes and synthesized under a medium to low pressure with a transition metal catalyst, can not satisfy all the requirements of processability, mechanical strengths and transparency. For instance, lowering of molecular weight for improvement of processability results in large reduction in mechanical strengths and disappearance of said copolymer characteristics. Broadening of molecular weight distribution leads to large reduction in mechanical strengths as well (cf. Reference example 2.), and moreover transparency worsens and surfaces of molded products get sticky. Thus, both of processability and physical properties are not met together yet, and any low density ethylene-α-olefin copolymer excellent in processability and mechanical strengths have not yet been provided.

As described above, high pressure polyethylenes are excellent in rheology characteristics and processability but poor in mechanical strengths. On the other hand, ethylene-α-olefin copolymers polymerized under a medium to low pressure with a transition metal catalyst and having densities about equal to those of high pressure polyethylenes, have excellent mechanical strengths due to their narrower molecular weight distributions but are poor in processability. These property differences are considered to originate from molecular structures of polymers.

High pressure polyethylenes are obtained from radical polymerization under a pressure of about 1500 to 4000 kg/cm² at a temperature of about 150° to 350° C. in an autoclave or a tubular reactor. Their molecular structures are very complicated and, in spite of being homopolymers of ethylene, have short chain branches which are alkyl groups of 1 to 6 carbon atoms. These short chain branches affect crystallinities and therefore densities of polymers. The distribution of short chain branching of high pressure polyethylenes is relatively even, and both lower molecular weight components and higher molecular weight components have almost similar numbers of branches.

Another important feature of high pressure polyethylenes is that the polyethylenes also have long chain branches in complicated structures. Identification of these long chain branches is difficult, but these branches are considered to be alkyl groups of which lengths vary from about lengths of main chains to lengths having carbon atoms of over several thousands. The presence of these long chain branches largely affects melt rheology characteristics of polymers and this is one of the reasons for the excellent processability of high pressure method polyethylenes.

On the other hand, ethylene-α-olefin copolymers synthesized under a medium to low pressure with a transition metal catalyst and having densities about equal to those of high pressure polyethylenes, are obtained by copolymerizing ethylene and an α-olefin under a medium to low pressure of about 5 to 150 kg/cm² and at 0°–250° C. normally at a relatively low temperature of 30° to 200° C. with a transition metal catalyst in an autoclave or a tubular reactor. Their molecular structures are relatively simple. These ethylene-α-olefin copolymers seldom possess long chain branches and have only short chain branches. These short chain branches are not formed through complicated reaction processes as so in high pressure polyethylenes, but are controlled by the kind of an α-olefin to be used in the copolymerization. As an example, in a copolymerization between ethylene and butene-1, short chain branches formed are normally ethyl branches. These branches could be hexyl branches as a result of dimerization of butene-1. Short chain branches formed control crystallinities and densities of polymers.

Distribution of short chain branches is also affected by the nature of a transition metal catalyst used in the copolymerization, the type of polymerization and the temperature of polymerization. Different from the case of high pressure polyethylenes, the distribution is wide. Namely, as a general trend, lower molecular weight components have larger S.C.B. and higher molecular weight components have smaller S.C.B. (cf. Reference example 1.)

Ethylene-α-olefin copolymers obtained by copolymerizing ethylene and an α-olefin under a medium to low pressure with a transition metal catalyst and having

densities about equal to those of high pressure polyethylenes, have come to be practically used. Therefore, the conventional classification that polyethylene resins having densities of 0.910 to 0.935 g/cm³ fall in a category of high pressure polyethylenes, is improper and a new classification should be developed, mainly based on whether or not a polymer or resin has long chain branches. As low density polyethylenes substantially not having long chain branches, there are resins which are obtained by polymerization using a transition metal catalyst under a same high pressure and temperature as employed in the manufacture of high pressure method polyethylenes. These resins are also included in "ethylene-α-olefin copolymers" as defined by the present invention.

Presence or absence of long chain branches is clarified to a considerable extent by a theory of solution. As an example, the presence of long chain branches in an ethylene polymer can be known by using $[\eta]/[\eta]_l$ namely g_η^*. Herein, $[\eta]$ is the intrinsic viscosity of the ethylene polymer, and $[\eta]_l$ is the intrinsic viscosity of a reference linear polyethylene (high density polyethylene produced from homopolymerization of ethylene under a medium to low pressure with a Ziegler catalyst) having the same weight average molecular weight by the light scattering method. Molecules having more long chain branches have less spread in a solution, and therefore, their g_η^* is small. Normally, g_η^* of high pressure polyethylenes is 0.6 or less.

This method is useful, but practically presence of long chain branches can be known more easily and clearly by a correlation between melt index and intrinsic viscosity of polymer. This correlation was shown in Reference example 3. In there, the intrinsic viscosity of a high pressure polyethylene is far lower than that of the ethylene-α-olefin copolymer according to medium to low pressure method having the same melt index, because the former polyethylene has long chain branches.

Due to the difference of presence or absence of long chain branches, high pressure polyethylenes and ethylene-α-olefin copolymers give largely different properties in melt rheology characteristics, crystallinity, solid mechanical properties and optical properties.

The present inventors made strenuous efforts with an aim to obtain polyethylenes which will solve the above-mentioned defects of polyethylenes, will have processability equal to or better than that of high pressure polyethylenes, and will be excellent in tear strength, impact strength, environmental stress cracking resistance, low temperature resistance, creep characteristics, chemicals resistance, transparency and heat-sealing characteristics. As a result, the present inventors have found that, by mixing (a) an ethylene-α-olefin copolymer having a relatively higher molecular weight and of which density, intrinsic viscosity, S.C.B., kind of α-olefin and (weight average molecular weight)/(number average molecular weight) are specified and (b) another ethylene-α-olefin copolymer having a relatively lower molecular weight and of which density, intrinsic viscosity, S.C.B., kind of α-olefin and (weight average molecular weight)/(number average molecular weight) are specified, in such a way that the ratio of S.C.B. of the former copolymer over S.C.B. of the latter copolymer is in a specified range, ethylene copolymer compositions can be obtained which have extremely good processability compared with the conventional polyethylenes, as well as very excellent physical and chemical properties such as tear strength, impact strength, environmental stress cracking resistance, low temperature resistance, creep characteristics, chemicals resistance, transparency, and heat-sealing characteristics. The present inventors have also found that ethylene-α-olefin copolymer compositions substantially not having long chain branches and having a specific distribution of S.C.B. provide extremely good properties such as tensile strength, impact strength, environmental stress cracking resistance, low temperature resistance, creep characteristics, chemicals resistance, transparency and heat-sealing characteristics, compared with the conventional polyethylenes, and therefore, with such ethylene-α-olefin copolymer compositions, improvement of processability by broadening of molecular weight distribution can be attained without deterioration of properties described above. Thus, the present invention has been achieved.

According to the present invention, there is provided an ethylene-α-olefin copolymer composition excellent in strength and having a density of 0.910 to 0.940 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-olefine copolymer B; said copolymer A 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, and the number of short chain branching per 1000 carbon atoms (S.C.B.) of 7 to 40; 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, and S.C.B. of 5 to 35; 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 at least 0.6.

The present invention also provides a composition of copolymers of ethylene and an α-olefin of 3 to 18 carbon atoms, having the following properties:

(1) density of 0.910 to 0.940 g/cm³,

(2) intrinsic viscosity $[\eta]$ of 0.7 to 4.0 dl/g,

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

(4) the number of short chain branching per 1000 carbon atoms (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, and

(6) (S.C.B. of the higher molecular weight components)/(S.C.B. of the lower molecular weight components) being at least 0.6, wherein these two component groups are obtained by a molecular weight fractionation method.

The first feature of this invention is to provide an ethylene copolymer composition of which processability is about equal to or better than that of high pressure polyethylenes and of which physical and chemical properties such as tensile strength, impact strength, environmental stress cracking resistance, creep characteristics, tear strength, transparency, heat-sealing characteristics and chemicals resistance are very excellent.

The second feature of this invention is that, because the product of this invention is excellent in mechanical strengths, has a rigidity higher than those of high pressure polyethylenes and has a transparency about equal to that of high pressure polyethylenes, material saving can be expected with the product of this invention; for

instance, when this product is used for films, the same performance can be obtained with the thickness 10 to 20% thinner than that of high pressure polyethylenes.

The third feature of this invention is that, because the product of this invention has extrusion processability superior to that of relatively low density ethylene-α-olefin copolymers by the conventional technique, conventional extruders being used for high pressure polyethylenes can be utilized for the present product without any modification.

The fourth feature of this invention is that, because the present product, even if possessing a melt index lower than that of low density ethylene-α-olefin copolymers by the conventional technique, shows satisfactory flow properties in actual processing, it gives excellent bubble stability and mechanical strengths of machine and transverse directions can be easily balanced, whereby molded products can have a uniform quality.

The fifth feature of this invention is that, because a resin composition less sticky then low density ethylene-α-olefin copolymers by the conventional technique is obtained even when the density of the composition is lowered, the composition can be applied even for the usages where transparency, flexibility and impact characteristics are required.

BRIEF DESCRIPTION OF THE DRAWINGS

In the attached drawings,

FIGS. 1 to 6 show curves of molecular weight distributions obtained from gel permeation chromatography. Broken lines in these figures are for dividing lower molecular weight components and higher molecular weight components into two respective territories.

FIG. 7 is a typical example showing "distribution of S.C.B against molecular weight" of an ethylene-α-olefin copolymer of the conventional technique.

FIG. 8 shows correlations between melt indices (MI) and tensile impact strengths of ethylene-α-olefin copolymers of the conventional technique, with their melt flow ratios (MRF) used as a parameter.

FIG. 9 shows correlations between MI and intrinsic viscosities [η] of a high pressure polyethylene and a linear polyethylene of the medium to low pressure method as a method for distinguishing these two polymers. In the figure, a broken line is drawn to separate two territories, the left side territory is for the high pressure polyethylene of the conventional technique and the right side territory is for the linear polyethylene of the medium to low pressure method.

The present invention will be explained in more detail below.

An ethylene-α-olefin copolymer of a relatively high molecular weight (hereinafter referred to as "copolymer A") which is used in the present invention as one mixing component, is a copolymer of ethylene and an α-olefin of 3 to 18 carbon atoms. This α-olefin is one represented by the general formula $R—CH=CH_2$ wherein R is an alkyl group of 1 to 16 carbon atoms. Examples of the α-olefin include propylene, butene-1, pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, 4-methyl-pentene-1, 4-methyl-hexene-1 and 4, 4-dimethylpentene-1. Among these olefins, α-olefins of at least 4 carbon atoms are preferred. Particularly, butene-1, pentene-1, hexene-1, octene-1 and 4-methyl-pentene-1 are preferred from the standpoints of monomer availability, copolymerizability and quality of polymer obtained. These α-olefins can be used alone or in combination of two or more. The density of the copolymer A is influenced by the kind of an α-olefin used, the content of the olefin and the intrinsic viscosity of the copolymer. For the object of this invention, the density is required to be 0.895 to 0.935 g/cm³ and more preferably 0.895 to 0.930 g/cm³. At a density smaller than 0.895 g/cm³, copolymers stick to the reactor walls, making polymerization difficult, or, the density of the relatively lower molecular weight copolymer (namely "copolymer B" which is described later and used as another mixing component in the present invention) is required to be raised, resulting in formation of polymer compositions of undesirable qualities such a films of poor transparency. In the density higher than 0.930 g/cm³, the content of the α-olefin in the copolymer A becomes very low, and the copolymer A of such a high density does not give satisfactory mechanical strengths. For instance, in films, balancing of MD and TD strengths becomes difficult and heat-sealing characteristics get worse. S.C.B. in the copolymer A is preferably 7 to 40 and more preferably 10 to 40. (When R in the above α-olefin formula is a linear alkyl group, the number of methyl groups at branch ends per 1000 carbon atoms is S.C.B. When R is an alkyl group with a branch or branches, for instance, the α-olefin is 4-methyl-pentene-1, the branch is isobutyl group and the half number of methyl groups at the branch ends in S.C.B.) Short chain branching in ethylene-α-olefin copolymers occurs due to α-olefins and it hinders crystallization mainly of ethylene sequences and lowers densities. These effects vary depending upon the kind of α-olefin. Short chain branching is considered to also make some contribution to formation of interlamella molecules, and ultimately affects mechanical strengths and thermal properties of copolymers obtained. Therefore, when S.C.B. is below 7, mechanical strengths and heat-sealing properties of the composition become poor. For instance, in films, balancing of MD and TD strengths is difficult. When S.C.B. is over 40, there occur problems in polymerization of the copolymer A. Also the transparency of polymer compositions obtained from the copolymer becomes poor.

The molecular weight of the copolymer A is generally preferred to be 1.2 to 6.0 dl/g as intrinsic viscosity and more preferred to be 1.2 to 4.5 dl/g. When the intrinsic viscosity is below 1.2 dl/g, mechanical strengths of polymer compositions of the present invention are reduced. In over 6.0 dl/g, mixing with the copolymer B becomes difficult, and polymer compositions obtained have fish eyes and further worsened flow properties, as well as reduced transparency. In injection molding, the intrinsic viscosity is preferably 1.2 to 4.0 dl/g and more preferably 1.2 to 3.0 dl/g. If it is less than 1.2 dl/g, mechanical strengths of compositions are lowered. If it is over 4.0 dl/g, mixing with the copolymer B becomes insufficient, and polymer compositions obtained have fish eyes, deteriorated flow properties (tend to cause flow marks) and reduced transparency.

(Weight average molecular weight)/(number average molecular weight) of the copolymer A which is a measure for the molecular weight distribution of the copolymer obtained from gel permeation chromatography (hereinafter abbreviated as "GPC"), is preferably 2 to 10 and more preferably 3 to 8. If it is less than 2, such a copolymer A is difficult to produce. If it is over 10, polymer compositions have lower mechanical strengths and, when processed into films, cause blocking.

An ethylene-α-olefin copolymer of a relatively low molecular weight (hereinafter abbreviated as "copolymer B") which is used in the present invention as another mixing component, is a copolymer of ethylene and an α-olefin of 3 to 18 carbon atoms. As α-olefins, there may be selected the α-olefins used in the copolymer A. The density of the copolymer B is normally preferred to be 0.910 to 0.955 g/cm³. More preferrably, it is 0.915 to 0.953 g/cm³. When the density is below 0.910 the copolymer compositions possess reduced mechanical strengths and cause blocking due to bleeding of lower molecular weight components of low density on film surfaces. When the density is over 0.955 g/cm³, copolymer compositions of this invention possess worsened transparency and too high densities. In the area of injection molding, the density of the copolymer B is preferred to be 0.910 to 0.950 g/cm³ and more preferred to be 0.915 to 0.948 g/cm³. When the density is below 0.910 g/cm³, mechanical strengths of compositions are reduced and surface tackiness occurs. When the density is over 0.950 g/cm³, compositions have too high densities. S.C.B. of the copolymer B is preferred to be 5 to 35 and more preferred to be 7 to 30. When S.C.B. is below 5, the copolymer B has a lower molecular weight as a whole and its crystallization speed is fast, resulting in poor transparency of compositions. In case of over 35, reduction in mechanical strengths as well as blocking in films occurs.

The molecular weight of the copolymer B is 0.3 to 1.5 dl/g preferrably 0.4 to 1.5 dl/g as intrinsic viscosity. When the intrinsic viscosity is less than 0.3 dl/g, mechanical strengths and transparency of compositions are reduced. In case of over 1.5 dl/g, fluidity of compositions is poor. In the area of injection molding, the molecular weight of the copolymer B is preferrably 0.3 to 1.2 dl/g as intrinsic viscosity and more preferrably 0.4 to 1.2 dl/g. When the intrinsic viscosity is below 0.3 dl/g, mechanical strengths and transparency of compositions are reduced. In case of over 1.2 dl/g, fluidity of compositions is poor.

The value of (weight average molecular weight)/(number average molecular weight), namely, Mw/Mn of the copolymer B determined by gel permeation chromatography (GPC) is preferrably 2 to 10 and more preferrably 3 to 8. When Mw/Mn is below 2, the copolymer B is difficult to produce. When over 10, mechanical strengths of the compositions are reduced and surface tackiness of films occurs.

The copolymer A and the copolymer B as mentioned above can be obtained by copolymerizing ethylene and an α-olefin of 4 to 18 carbon atoms under a medium to low pressure using a transition metal catalyst. For instance, catalysts such as Ziegler type catalyst and Phillips type catalyst as well as polymerization methods such as slurry polymerization, gas phase polymerization and solution polymerization are used. As catalysts, a Ziegler type catalyst system using a carrier-supported Ziegler catalyst component is convenient in this invention from its activity and copolymerizability. Specific examples of an effective carrier of this carrier-supported Ziegler catalyst component include oxides, hydroxides, chlorides and carbonates of metals and silicon and their mixtures as well as inorganic complexes. More specifically, they are magnesium oxides, titanium oxides, silica, alumina, magnesium carbonates, divalent metal hydroxychlorides, magnesium hydroxides, magnesium chlorides, magnesium alkoxides, magnesium haloalkoxides, double oxides of magnesium and aluminum and double oxides of magnesium and calcium. Among these compounds, magnesium compounds are particularly preferred. The following magnesium compounds are particularly preferred. The following magnesium compound carrier is most preferred in the production of the low density polyethylene type resin composition of this invention, because it gives a satisfactory slurry with no abnormal tackiness and there occurs no sticking of polymers to the reactor wall. (Reference is made to Japanese Patent Publication No. 23561/1980.) Namely, it is the carrier obtained by (a) reacting in a solvent an aluminum halide represented by the general formula R_nAlX_{3-n} (R is an alkyl, aryl or alkenyl group of 1 to 20 carbon atoms and X is a halogen atom and n is an integer of 0 to 3) and/or a silicon halide represented by the general formula $R_m'SiX_{4-m}$ (R' is an alkyl, aryl or alkenyl group of 1 to 20 carbon atoms and X is a halogen atom and m is an integer of 0 to 4) with an organomagnesium compound represented by the general formulas R"MgX and/or $R_2"Mg$ (R" is an alkyl, aryl or alkenyl group of 1 to 20 carbon atoms and X is a halogen atom), and (b) isolating the solid product formed.

As a transition metal catalyst component supported on carriers, there are, for instance, titanium compounds, vanadium compounds and zirconium compounds. Specific examples include titanium tetrachloride, titanium tetrabromide, titanium tetraiodide, titanium trichloride, titanium alkoxy halides or titanium aryloxy halides represented by the general formula $Ti(OR^1)_{4-p}X_p$ (where R^1 is a hydrocarbon group, X is a halogen atom and p is an integer of $0<p<4$), vanadium tetrachloride, vanadium oxy trichloride, zirconium tetrachloride and zirconium alkoxy halides or zirconium aryloxy halides represented by the general formula $Zr(OR^2)_{4-q}X_q$ (where R^2 is a hydrogen group, X is a halogen atom and q is an integer of $0<q<4$). Among these compounds, titanium compounds and/or vanadium compounds are particularly preferred in the production of the low density polyethylene type resin composition of this invention, because they give satisfactory slurries with no abnormal tackiness and there occurs almost no sticking of polymers to the reactor wall. (Reference is made to Japanese Patent Publication No. 23561/1980.) Titanium compounds are most preferred from the standpoints of weather resistance and heat resistance.

As a component of carrier-supported Ziegler catalysts used in this invention, there are also reaction products between an organomagnesium compound and a transition metal compound. Here, the transition metal compound is represented by the general formula $Ti(OR^3)_{4-r}X_r$ (where R^3 is a hydrocarbon group, X is a halogen atom and r is an integer of $0 \leq r \leq 4$, and includes titanium tetrahalides, titanium alkoxides, titanium aryloxides, titanium alkoxy halides and titanium aryloxy halides.

As an organometal compound component which forms the catalyst system of this invention together with the carrier-supported Ziegler catalyst component, there are organoaluminum compounds such as trialkyl aluminums (triethyl aluminum, tri-n-propyl aluminum, tri-i-butyl alminum, tri-n-butyl aluminum, tri-n-hexyl aluminum, etc.), dialkyl aluminum monohalides (diethyl aluminum monochloride, di-n-propyl aluminum monochloride, di-i-butyl aluminum monochloride, di-n-butyl aluminum monochloride, di-n-hexyl aluminum monochloride, etc.), alkyl aluminum dihalides (ethyl aluminum dichloride, n-propyl aluminum dichloride, i-butyl

aluminum dichloride, n-butyl aluminum dichloride, n-hexyl aluminum dichloride, etc.), ethyl aluminum sesquichloride, i-propyl aluminum sesquichloride, i-butyl aluminum sesquichloride, n-butyl aluminum sesquichloride and n-hexyl aluminum sesquichloride as well as other organometal compounds such as organozinc compounds. These organometal compounds may be used alone or in combination of two or more.

In compounding the composition of this invention using the ethylene-α-olefin copolymer A of relatively higher molecular weight and the ethylene-α-olefin copolymer B of relatively lower molecular weight both of which are obtained with the above catalyst system under a normal medium to low pressure polymerization method, the following matters must be obeyed.

(1) From the standpoint of mechanical strengths, the copolymers A and B must be selected in order that (S.C.B. of copolymer A)/(S.C.B. of copolymer B) becomes at least 0.6, preferably at least 0.8 and more preferably at least 1.0. Meanwhile, from the standpoint of transparency, it is necessary that (S.C.B. of copolymer A)/(S.C.B. of copolymer B) is 0.6 to 1.7. When this ratio is below 0.6, mechanical strengths of the copolymer composition obtained are reduced. In films, for instance, balancing of MD and TD strengths is difficult, heat-sealing characteristics worsen and tackiness is seen. In case of over 1.7, transparency of the copolymer composition is reduced.

(2) The density of the copolymer composition is normally preferred to be 0.910 to 0.940 g/cm^3 and more preferred to be 0.915 to 0.935 g/cm^3 and most preferred to be 0.915 to 0.929 g/cm^3. When the density is below the above lower limit, mechanical strengths of the composition is reduced and, in case of films, tackiness is seen. When the density is above the upper limit, transparency of the composition worsens.

In the field of extrusion processing, the density of the copolymer composition is preferred to be 0.910 to 0.930 g/cm^3 and more preferred to have 0.915 to 0.929 g/cm^3. When the density is below the lower limit, mechanical strengths of the composition is reduced and products have tackiness. When the density is above the upper limit, transparency worsens.

In the field of film processing, the density of the copolymer composition is preferred to be 0.910 to 0.940 g/cm^3 and more preferred to be 0.915 to 0.935 g/cm^3 and most preferred to be 0.915 to 0.929 g/cm^3. When the density is below the lower limit, mechanical strengths of the composition are reduced and films possess tackiness. When the density is above the upper limit, transparency worsens.

In the field of injection molding, the density of the copolymer composition is preferred to be 0.910 to 0.935 g/cm^3 and more preferred to be 0.915 to 0.929 g/cm^3. When the density is below the lower limit, mechanical strengths of the composition is reduced and molded products have tackiness. When the density is above the upper limit, transparency worsens.

(3) The melt index of the copolymer composition is normally preferred to be 0.02 to 50 g/10 min. and more preferred to be 0.05 to 40 g/10 min. and most preferred to be 0.1 to 30 g/10 min. In addition, the melt flow ratio is preferred to be 35 to 250 and more preferred to be 35 to 200 and most preferred to be 35 to 150. Furthermore, the product of the melt index and the melt flow ratio is preferred to be at least 4 and more preferred to be at least 7. When the melt index and the melt flow ratio are below the lower limits, extrusion processability worsens. When they are above the upper limits, bubble stability in blown film processing is lost and mechanical strengths are reduced.

In the field of extrusion processing, the MI of the copolymer composition is preferred to be 0.02 to 2.0 g/10 min. and more preferred to be 0.05 to 2.0 g/10 min. and most preferred to be 0.10 to 2.0 g/10 min. Further, the MFR is preferred to be 35 to 250 and more preferred to be 35 to 200 and most preferred to be 35 to 150. Furthermore, the product of MI and MFR is preferred to be at least 4 and more preferred to be at least 7. When the MI and the MFR are below the lower limits, extrusion processability worsens. When they are above the upper limits, mechanical strengths are reduced.

In the field of film processing, the MI of the composition is preferred to be 0.02 to 5 g/10 min. and more preferred to be 0.05 to 4 g/10 min. and most preferred to be 0.1 to 3 g/10 min. Further, its MFR is preferred to be 35 to 250 and more preferred to be 35 to 200 and most preferred to be 35 to 150. Furthermore, the product of the MI and the MFR is preferred to be at least 4 and more preferred to be at least 7. When the MI and the MFR are below the lower limits, extrusion processability worsens. When they are above the upper limits, bubble stability in blown film processing is insufficient and mechanical strengths are reduced.

In the field of injection molding, the MI of the composition is preferred to be 2.0 to 50 g/10 min. and more preferred to be 2.0 to 30 g/10 min. Further, the MFR is preferred to be 35 to 80 and more preferred to be 35 to 70. When the MI is below the lower limit, moldability worsens and flow marks are produced. When it is above the upper limit, mechanical strengths are reduced.

In order to provide the composition of this invention excellent in processability and mechanical strengths, it is also important to adequately balance its MI and MFR. A lower MI requires a higher MFR. This requirement is expressed by the product of MI and MFR. For instance, a composition having a MI of about 1 g/10 min, even if its MFR is as low as 50 to 60, has processability about equal to that of a high pressure polyethylene having the same MI. On the other hand, a composition having a MI of about 0.05 g/10 min. and a MFR of 50 possesses extremely poor processability and, in order to have satisfactory processability, a MFR of at least 80 is required. The product of MI and MFR of a composition is designed appropriately to meet the requirement of its final application. The designed value of the product of MI and MFR can be achieved in the composition by using (a) intrinsic viscosities of the copolymer A of relatively higher molecular weight and the copolymer B of relatively lower molecular weight, (b) values of (weight average molecular weight)/(number average molecular weight) of these copolymers and (c) their mixing ratio. If intrinsic viscosities of the copolymer A and the copolymer B are put as $[\eta]_A$ (dl/g) and $[\eta]_B$ (dl/g), respectively, and their ratios by weight basis are put as W_A and W_B ($W_A+W_B=1$), respectively the intrinsic viscosity of the composition obtained by mixing the two copolymers namely $[\eta]_T$(dl/g) is approximately given by the following formula.

$$[\eta]_T=[\eta]_A W_A+[\eta]_B W_B$$

MI is governed by $[\eta]_T$ unequivocally. Meanwhile, MFR is generally larger when $[\eta]_A/[\eta]_B$ is larger, and depends upon W_A and W_B. Therefore, it is difficult to express MFR unequivocally and, based on preliminary

tests. $[\eta]_A$, $[\eta]_B$, W_A and W_B are determined to give an intended MFR.

(4) In order to obtain a composition which satisfies the above (1) to (3) conditions, the copolymer A and the copolymer B are preferred to be mixed at a ratio of 10 to 70% by weight (copolymer A) to 90 to 30% by weight (copolymer B). The ratio of 20 to 65% by weight to 80 to 35% by weight is more preferred and the ratio of 30 to 60% by weight to 70 to 40% by weight is most preferred. The mixing ratio of the two copolymers must be adequately selected by considering S.C.B., densities, intrinsic viscosities and molecular weight distributions of the copolymers A and B as well as the density, MI and MFR of an intended composition. When the ratio of the copolymer A is below its lower limit and the ratio of the copolymer B is above its upper limit, the ESCR, impact strength, tear strength and low temperature resistance of the composition obtained are poor, and the high strength of the composition of this invention which is obtained when the value of (S.C.B. of copolymer A)/(S.C.B. of copolymer B) is selected to be at least 0.6 as well as the good transparency of the composition of this invention which is obtained when the value of (S.C.B. of copolymer A)/(S.C.B. of copolymer B) is selected to be 0.6 to 1.7, are not achieved. When the ratio of the copolymer A is above its upper limit and the ratio of the copolymer B is below its lower limit, the processability of the composition obtained worsens.

As long as the scope of this invention is obeyed, mixing of the ethylene-α-olefin copolymer A of relatively higher molecular weight and the ethylene-α-olefin copolymer B of relatively lower molecular weight is not necessarily limited to mixing one of each kind. The mixing may be also done by using two or more kinds of each of the copolymer A and the copolymer B.

There is no particular limitation to mixing methods of the copolymers A and B, and known methods can be used in mixing of these two polymers. Commonly used are a batch type melt kneading method which employs a twin roll or a Banbury mixer after separate production of the copolymers A and B, a continuous melt kneading method employing a twin rotor mixer such as CIM (manufactured by the Japan Steel Works) or FCM (manufactured by Kobe Steel) or a single screw extruder and a solution mixing method in which a mixture is obtained by dissolving the copolymers A and B in a solvent separately or together, blending and finally removing the solvent. When the copolymers A and B are produced by a high temperature solution polymerization method, it is advantageous from the process standpoint that their composition is obtained by mixing A and B in a solution state at high temperatures and removing the solvent.

Mixing by a two- or multi-stage polymerization method is also possible. In this method, in the first stage, the copolymer A is polymerized for a certain length of time and, successively in the second stage, the copolymer B is polymerized using the same catalyst but changing other polymerization conditions until the composition containing the copolymers A and B at an intended ratio is obtained. In this case, the order of polymerization of A and B is not restricted.

The above two- or multi-stage polymerization method is an ideal mixing method, because the copolymers A and B undergo molecular dispersion.

The most effective mixing method can be selected from above various mixing methods, in order to obtain a uniform composition, which meets intended requirements.

The intrinsic viscosity $[\eta]$ of the ethylene-α-olefin copolymer composition of this invention is preferred to be 0.7 to 4 dl/g and more preferred to be 0.8 to 3.5 dl/g and most preferred to be 0.9 to 3 dl/g. When the intrinsic viscosity is below the lower limit, mechanical strengths are reduced and, in blown film processing, bubble stability is insufficient. In case of above the upper limit, extrusion processability worsens.

S.C.B. of the composition is preferred to be 5 to 45 and more preferred to be 7 to 40 and most preferred to be 10 to 40. When S.C.B. is below its lower limit, transparency worsens. When S.C.B. is above its upper limit, mechanical strengths are reduced and molded products have tackiness.

Next, the "index of long chain branching" of the copolymer composition of this invention is described. When the intrinsic viscosity of a copolymer composition of this invention is put as $[\eta]$ and the intrinsic viscosity of a linear polyethylene having the same Mw measured by light scattering method (a high density polyethylene obtained by homopolymerization of ethylene under a medium to low pressure using a Ziegler catalyst) is put as $[\eta]_L$, $[\eta]/[\eta]_L$ namely g_η^* is called the "index of long chain branching" of the composition and indicates the extent of presence of long chain branching in the composition. Now, intrinsic viscosities of two polymers are compared. One polymer X is a polyethylene having long chain branches of which index of branching is unknown (for instance, a high pressure polyethylene) and the other polymer is a linear polyethylene containing no long chain branches but having the same Mw measured by light scattering method. When these two polymers are made into respective very dilute solutions with one same solvent, the polymer X gives a less-viscous solution because the spread of its molecular chain is smaller than that of the linear polyethylene. Accordingly, by measuring the intrinsic viscosities of the two polymers and calculating their ratio namely g_η^*, the index of long chain branching can be known. When a polymer has no long chain branches, its g_η^* is almost 1 within the range of experimental errors. When the polymer has long chain branches, g_η^* is smaller than 1. In most cases, high pressure polyethylenes show g_η^* of below 0.6 and have considerable quantities of long chain branches.

The ethylene-α-olefin copolymer composition of this invention is preferred to have g_η^* of at least 0.8 and more preferably at least 0.9 and practically has no long chain branches. When g_η^* is below 0.8 and contain a large quantity of long chain branches, the copolymer is poor in tensile strength, impact strength, environmental stress cracking resistance, low temperature resistance and chemicals resistance.

(S.C.B. of higher molecular weight components)/(S.C.B. of lower molecular weight components) of the copolymer composition of this invention is preferred to be at least 0.6 and more preferred to be at least 0.8 and most preferred to be at least 1.0. In applications where transparency is required, 0.6 to 0.8 is preferred. Here, these S.C.B. are obtained by dividing the composition of this invention into two groups of lower molecular weight components and higher molecular weight components using molecular weight fractionation and then measuring S.C.B. of each group. When the ratio is below 0.6, mechanical strengths of the composition are poor, and when the composition is

subjected to extrusion processing and injection molding, balancing of MD and TD strengths is difficult and molded products have sticky surfaces, and in films, heat-sealing characteristics worsen. When the ratio is over 0.8, transparency worsens and therefore such a polymer is not suitable for applications where transparency is required. The above molecular weight fractionation of the ethylene-α-olefin copolymer into two groups of lower and higher molecular weight components refers to the following method.

(1) A curve of molecular weight distribution is obtained by gel permeation chromatography.

In this case, the abscissa is the logarithm of chain length (unit Å) calibrated with a standard polystyrene sample, and the ordinate is relative weight fraction. The standard measurement method is described later.

(2) An example of cases where curves of molecular weight distributions have one peak was shown in FIG. 1. This pattern is seen most typically in etnylene-α-olefin copolymers. In this case, a lower molecular weight components side and a higher molecular weight components side are divided by a line drawn between the peak of the curve and the midpoint of a line drawn between the end of lower molecular weight components in the curve and the end of higher molecular weight components; and the ratio of areas of these two sides is the weight ratio of lower and higher molecular weight components. Separately, fractions of the same sample are prepared by column fractionation. These fractions are consolidated into two portions of lower and higher molecular weight components, in order that the weight ratio of these two portions become closest to the weight ratio obtained above.

(3) An example of cases where curves of molecular weight distributions have two peaks was shown in FIG. 2. Also, an example having one peak but showing a shoulder at higher molecular weight components side was shown in FIG. 3. Examples having three or more peaks are handled as modifications of two peaks and are treated similarly to two peaks. In the case of two or more peaks including shoulders, a tangent line is drawn between main two peaks of the higher molecular weight components side or between one peak and a shoulder of the same side, and then a perpendicular is drawn from a point where the distance between the GPC curve and the tangent line becomes largest. This perpendicular splits the lower molecular weight components side and the higher molecular weight components side, and the ratio of areas of these two sides becomes the weight ratio of these two components portions. When peaks are continuous and can not be detected (case of somewhat square curve), the technique of one peak distribution is applied. Separately, fraction of the same sample are prepared by column fractionation. These fractions are consolidated into two portions of lower and higher molecular weight components, in order that the weight ratio of these two portions becomes closest to the weight ratio thus obtained.

Molecular weight fractionation is conducted by the known column fractionation method. Its detailed explanation is made in "Polymer Fractionation" (compiled by M. J. R. Cantow, Academic Press, published in 1967), and therefore, only the outline of the method is described below.

About 5 g of a sample is adsorbed on a carrier, Celite 745, in xylene and the carrier is charged into a column. The column is heated to 130° C. and a mixed solvent of butyl cellosolve and xylene is passed through the column with their mixing ratio being gradually changed (namely with the solvency of the mixed solvent being gradually changed). The lower molecular weight fractions to higher molecular weight fractions are successively fractionated. To each eluate is added methanol to cause precipitation. After recovery of each polymer, they are dried under reduced pressure to be used as each fraction. To prevent the decomposition of polymers during fractionation, 100 ppm of Irganox ®1076 is added to the original sample as a stabilizer, and also nitrogen is passed through the column to shut off oxygen. The polymer fractions obtained are divided into two groups of lower and higher molecular weight components so that the weight ratio of these two groups become the abovementioned weight ratio. Each group is made into a press sheet of about 100 to 300μ thickness and these sheets are subjected to Fourier-transform infra-red absorption spectroscopy.

Further, it is preferable that the characteristic values of the sample obtained by dividing the ethylene-α-olefin copolymer of this invention into two fractions such as a higher molecular weight component and a lower molecular weight component are same to the characteristic values of copolymer A and copolymer B, respectively, as previously defined.

When compared with low density ethylene-α-olefin copolymers obtained from the conventional medium to low pressure method (normally called "linear low density polyethylene or LLDPE"), the polyethylene type resin composition of this invention has the following advantages.

In the field of extrusion processing, the composition of this invention is largely excellent in processability (about equal even to high pressure polyethylenes) and moreover has excellent mechanical strengths (ESCR, tensile strength, impact strength and tear strength) as well as excellent low temperature resistance. Therefore, reduction in thicknesses of molded products becomes possible. The composition of this invention has wide applications and can be used even in the application where transparency is required.

In case of films, the present composition is far superior in processability (about equal even to high pressure polyethylenes). Further, the composition has excellent mechanical strengths such as tensile strength, impact strength and tear strength, by which reduction in thicknesses of films becomes possible. Moreover, the present composition has excellent transparency and heat-sealing characteristics, by which it is used as a high quality film in wide applications including high speed bag manufacturing.

In the field of injection molding, the present composition is largely excellent in processability (about equal even to high pressure polyethylenes). Moreover, there occurs no flow marks, there is no warpage with molded products, and transparency, low temperature resistance and mechanical strengths such as environmental stress cracking resistance, tensile strength and impact strength are excellent. Thereby, reduction in thicknesses of molded products is possible and the present composition has wide applications including the case where transparency is required.

To the composition of this invention, can be added if necessary various additives being commonly used in the industries such as oxidation inhibitors, lubricants, anti-blocking agents, anti-static agents, photostabilizers, and coloring pigments. Also, other polymers can be added