Propylene random copolymer, method for its preparation, and compositions and articles containing the same

Technical Field

The present invention relates to a propylene random copolymer, a method for its preparation, and compositions and articles containing the same, wherein the propylene random copolymer is particularly a propylene-butene-1 random copolymer.

Background Art

Propylene random copolymer usually refers to a polymer obtained by randomly copolymerizing a small amount, usually not more than 15% by weight, of α-olefin monomer, for example, commonly used ethylene or butene-1, onto a polypropylene molecular chain. Since the comonomers destroy the regularity of the arrangement of the propylene units in the molecular chain, the melting point and the degree of crystallinity of the polypropylene resin are declined. The relatively low melting point enables the polypropylene resin to be used for manufacturing a more readily heat-sealable film and the like, while the relatively low degree of crystallinity results in improved transparency of the material. Although comonomers are often copolymerized in a larger amount in order to achieve higher transparency, the excessively increasing in the amount of comonomers may unduly reduce the degree of crystallinity of the material, thereby reducing the rigidity and heat resistance of the material, and more important also increase the content of the non-crystalline components (the soluble contents) in the material, so that they tend to migrate onto the surface of articles and thus affect negatively the processing and application of the product. In particular, in case that the product is used for packaging greasy foods, a part of the non-crystalline components may gradually migrate to the food, and contaminate it. In addition, reducing the melting point and the degree of crystallinity usually also render heat resistance of the material deteriorated. If such a material is used in food containers, the deteriorated heat resistance makes it disadvantageous

to the microwave heating. The use of comonomers in a unduly larger amount may also bring difficulties to the polymerization process, for example, the occurrence of kettle-sticking, caking and hard removal of residual monomers, in particular when the conomomer is butene-1 having higher boiling point or α-olefins having more carbon atoms.

In the prior art, butene-1 and propylene are often used to carry out random copolymerization, with the expectation that the resultant propylene-butene-1 random copolymer has a relatively low migrants content. However, the random copolymer still has drawbacks in giving consideration to both transparency and heat resistance. An existing solution is to combine with an appropriate amount of nucleating agent that can improve the transparency. Although this can, to some extent, improve the transparency and heat resistance of the copolymer material, the result is still not satisfactory in terms of the heat resistance and the migrants content.

Contents OF THE INVENTION

Therefore, one object of the present invention is to provide a propylene-butene-1 random copolymer, which is featured with good heat resistance and low xylene soluble content at room temperature, while maintaining or even further improving the excellent transparency.

By experiments, the present inventors have surprisingly found that, by increasing the relative dispersity of butene-1, the material can achieve at least the same transparency, but better heat resistance.

In the process of randomly copolymerizing butene-1 as a comonomer with propylene, if a higher proportion of butene-1 monomers is inserted into the polypropylene molecular chain as discretely arranged monomer units, and a lower proportion of butene-1 monomers is inserted into the polypropylene molecular chain as consecutively arranged monomer units (such as BB dual units or more consecutive monomer units), the ratio of the observed dispersion coefficient

$MD_{observed(B)}$ of butene-1 unit in the molecular chain to the ideal random dispersion coefficient $MD_{random(B)}$ will be greater. This ratio is defined as the relative dispersity $MD_{relative(B)}$ of butene-1, which is calculated according to the following equation:

$$MD_{observed(B)} = \frac{\frac{1}{2}[PB]}{[B]} \times 100 \quad (1)$$

$$MD_{random(B)} = (1 - [B]) \times 100 \quad (2)$$

$$MD_{relative(B)} = \frac{MD_{observed(B)}}{MD_{random(B)}} \times 100 \quad (3)$$

Wherein, [PB] represents the number of butene-1 monomeric units linked to propylene monomeric units in the molecular chain; [B] represents the total number of butene-1 monomeric units in the molecular chain; and $MD_{observed(B)}$, $MD_{random(B)}$ and $MD_{relative(B)}$ are calculated in unit %.

Another object of the present invention is to provide a method for preparing propylene-butene-1 random copolymer. The method is capable of preparing propylene-butene-1 random copolymer with a very high relative dispersity of butene-1 and a low xylene soluble content at room temperature. Moreover, the polymerization process is easy to operate, and can avoid the occurrence of kettle-sticking, caking, hard removal of residual monomers and the like.

Still another object of the present invention is to provide a polypropylene composition, in particular a propylene-butene-1 random copolymer composition, which has high transparency, low migrants content and high heat resistance.

Still another object of the present invention is to provide a food packaging container, which has high transparency, low migrants content and high heat resistance.

In addition, the present invention also provides methods for preparing the

polypropylene composition and the food packaging container as described above.

The propylene-butene-1 random copolymer in the present invention has a butene-1 content of 1-6 mol%, preferably 3-6 mol%, and has a relative dispersity of butene-1, as determined according to NMR method, of greater than 98.5%, preferably greater than 99.0%.

The butene-1 content in the propylene-butene-1 random copolymer may affect the degree of crystallinity of polypropylene. The higher the butene-1 content is, the lower the degree of crystallinity of polypropylene will be, and the better the transparency of the material will be. However, an excessively high butene-1 content may result in excessive xylene solubles at room temperature, while an excessively low butene-1 content may result in a excessively high degree of crystallinity which influences the transparency. By a large number of experiments, it has been found that the butene-1 content is preferably 1-6 mol%, more preferably 3-6 mol%.

As mentioned above, by increasing the relative dispersity of butene-1 in the propylene-butene-1 random copolymer, the material may have better heat resistance while achieving the same transparency. The relative dispersity of butene-1 in the propylene-butene-1 random copolymer of the present invention can be up to greater than 98.5%, preferably greater than 99.0%.

Due to a very high relative dispersity of butene-1, the propylene-butene-1 random copolymer of the present invention can have a heat distortion temperature up to above 90℃, preferably above 95℃.

The increase of the amount of comonomer in propylene random copolymer may usually lead to the increase of the xylene solubles content at room temperature, and such a result applies also to butene-1 as a comonomer. In general, a relatively high xylene solubles content at room temperature may result that the product as a packaging material is not allowed to be in direct contact with food, pharmaceutical and the like, or else, it may contaminate the packaged items. However, within the

butene-1 content range in the propylene-butene-1 random copolymer as suggested in the present invention, the xylene solubles content at room temperature increases slowly as the butene-1 content increases.

In concrete, the xylene solubles content at room temperature (about 25℃) in the propylene-butene-1 random copolymer of the present invention is lower than the following fitted line:

$Y = 0.77 + 0.252X$

Wherein: Y is the weight percent of xylene solubles at room temperature (e.g. in case of 5 wt%, Y = 5); X is the mole percent of butene-1 in the propylene-butene-1 random copolymer (e.g. in case of 5 mol%, X = 5).

Due to the reduction in the xylene solubles content at room temperature, the propylene-butene-1 random copolymer of the present invention, when used for food packaging containers, has higher food safety; and, when used for film processing, it is not easy to stick rollers and makes the metal plating layer not so easy to be detached.

Usually, the processability of the polymer is controlled by controlling the melt index. Preferably, the propylene-butene-1 random copolymer of the present invention has a melt index, as measured at 230℃ under a load of 2.16 kg, of 0.5-50 g/10 min, preferably 2-30 g/10 min.

The propylene-butene-1 random copolymer of the present invention has a molecular weight distribution index Mw/Mn for characterizing the molecular weight distribution, as measured according to GPC, of 3.5-8, preferably 3.8-6. A too small molecular weight distribution index means that the molecular weight distribution is narrow, so that the processing performance of the material becomes poor; and a too large molecular weight distribution index means that the molecular weight distribution is wide, so that the transparency of the material may be affected and reduced.

The propylene-butene-1 random copolymer of the present invention having a high relative dispersity of butene-1 in combination with better transparency and heat resistance is very suitable for packaging food that may be edible after heating. Moreover, the copolymer has such a lower xylene solubles content at room temperature that, when used as packaging material, it can advantageously avoid the contamination of the packaged items from the precipitation of room temperature solubles, and may be more suitable for using as food and pharmaceutical packaging materials.

The method for preparing the propylene-butene-1 random copolymer of the present invention comprises: the copolymerization of propylene and butene-1 is carried out by adjusting the amount of the comonomer butene-1 added in the reactor to obtain the propylene-butene-1 random copolymer in the presence of a selected Ziegler-Natta catalyst and at a polymerization temperature and an appropriate hydrogen content.

The selected Ziegler-Natta catalyst in the present invention refers to the catalysts as described in Chinese Patents CN85100997A, CN1258680A, CN1258683A, CN1258684A. The contents disclosed in the four documents are all incorporated herein as the technical solutions relating to the catalyst of the present invention and thus become a part of the present invention. The catalyst as described in Chinese patent CN1258683A particularly has advantages when used as the catalyst of the present invention, so the contents disclosed in this document are all incorporated herein as the preferred technical solution relating to the catalyst of the present invention.

In a specific embodiment, the propylene-butene-1 random copolymer is obtained by copolymerization with the use of a Ziegler-Natta catalyst comprising a main catalyst component A, a co-catalyst component B and an external electron donor component C,

wherein the main catalyst component A is a solid catalyst component comprising titanium and a polybasic carboxylic acid ester obtained by dissolving magnesium

halide in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent;
the component B is an alkyl aluminum compound having the general formula AlR_nX_{3-n}, wherein R is hydrogen or a hydrocarbon group having 1 to 20 carbon atoms, X is halogen; and
the component C is an organosilicon compound having the general formula $R_nSi(OR')_{4-n}$, where $0 \leq n \leq 3$, R and R' are the same or different alkyl groups, cycloalkyl groups, aryl groups or halogenated alkyl groups.

Preferably, in the solvent system as described above, based on per mole of the magnesium halide, the amount of the organic epoxy compound is 0.2-5 moles, and the mole ratio of the organic epoxy compound to the organic phosphorus compound is 0.9-1.6.

Preferably, the mole ratio of the component B to the component A, measured as the mole ratio of aluminum to titanium, is 5-1000, and the ratio of the component C to the component A, measured as the mole ratio of silicon to titanium, is 2-100.

The main catalyst component A may be, for example, obtained by dissolving magnesium halide in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent to form a homogeneous solution, then mixing the solution with titanium halide or a derivative thereof to precipitate a solid in the presence of a precipitating agent, treating the solid with a polybasic carboxylic acid ester to make it loaded on the solid, and then treating the solid with titanium tetrahalide and an inert diluent, wherein the precipitating agent is one selected from an organic acid anhydride, an organic acid, an ether and a ketone.

The further preferred Ziegler-Natta catalyst in the present invention is characterized in that it comprises a main catalyst component A, a co-catalyst component B and an external electron donor component C,
wherein the component A is a solid catalyst component comprising titanium,

obtained by dissolving magnesium halide in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent to form a homogeneous solution, mixing the solution with titanium halide or a derivative thereof to precipitate a solid in the presence of a precipitating agent, treating the solid with a polybasic carboxylic acid ester to make it loaded on the solid, and then treating the solid with titanium tetrahalide and an inert diluent, wherein the precipitating agent is one selected from an organic acid anhydride, an organic acid, an ether and a ketone and in the solvent system as described above, based on per mole of the magnesium halide, the amount of the organic epoxy compound is 0.2-5 moles, and the mole ratio of the organic epoxy compound to the organic phosphorus compound is 0.5-1.6;

the component B is an alkyl aluminum compound having the general formula AlR_nX_{3-n}, where R is hydrogen or a hydrocarbon group having 1 to 20 carbon atoms, X is halogen; and

the component C is an organosilicon compound having the general formula $R_nSi(OR')_{4-n}$, where $0 \leq n \leq 3$, R and R' are the same or different alkyl groups, cycloalkyl groups, aryl groups or halogenated alkyl groups;

the mole ratio of the component B to the component A, measured as the mole ratio of aluminum to titanium, is 5-1000, and the ratio of the component C to the component A, measured as the mole ratio of silicon to titanium, is 2-100.

The magnesium halide in the above catalyst component A includes magnesium dihalide, complexes of magnesium dihalide with water, alcohol and the like, and derivatives obtained by replacing one halogen atom in the molecular formula of magnesium dihalide with hydrocarbon group or halohydrocarbyloxy group. With respect to the magnesium dihalide as mentioned above, it can be magnesium dichloride, magnesium dibromide and magnesium diiodide.

The organic epoxy compound in the above catalyst component A includes aliphatic olefins having 2 to 8 carbon atoms, diolefins or halogenated aliphatic olefins or oxides of diolefins, glycidyl ethers, inner ethers and the like. As the concrete examples for the above list, the useful compound can be selected from ethylene

oxide, propylene oxide, butylene oxide, butadiene oxide, butadiene dioxide, epichlorohydrin, methyl glycidyl ether, diglycidyl ether, tetrahydrofuran.

The organic phosphorus compound in the above catalyst component A includes hydrocarbyl esters or halogenated hydrocarbyl esters of ortho-phosphoric acid or phosphorous acid. In concrete, such a compound can be, for example, trimethyl ortho-phosphate, triethyl ortho-phosphate, tributyl ortho-phosphate, triphenyl ortho-phosphate, trimethyl phosphite, triethyl phosphite, tributyl phosphite, benzyl phosphite.

The inert diluent in the above catalyst component A may include hexane, heptane, octane, benzene, toluene, xylene, 1,2-dichloroethane, chlorobenzene and other hydrocarbon or halogenated hydrocarbon compounds.

The magnesium halide solution in the above catalyst component A has the following composition: based on per mole of magnesium halide, the amount of the organic epoxy compound is 0.2-5 moles, preferably 0.5-2 moles; the mole ratio of the organic epoxy compound to the organic phosphorus compound is 0.5-1.6, preferably 0.9-1.6, most preferably 0.9-1.4; and the amount of the inert diluent is 1200-2400 ml, preferably 1400-2000 ml.

The halide of transition metal Ti or its derivative in the above catalyst component A is represented by the general formula $TiX_n(OR)_{4-n}$, where n = 1-4. In concrete, the examples of such compounds may be titanium tetrachloride, titanium tetrabromide, titanium tetraiodide, tetrabutoxy titanium, tetraethoxy titanium, monochloro triethoxy titanium, dichloro diethoxy titanium, and trichloro monoethoxy titanium. The amount of the halide of transition metal Ti or its derivative is 0.5-150 moles, preferably 1-20 moles, per mole of magnesium halide.

The precipitating agent in the above catalyst component A is selected from the group consisting of organic acids, organic acid anhydrides, organic ethers, organic ketones, or mixtures thereof. As examples for the above list, the precipitating agent

can be selected from acetic anhydride, phthalic anhydride, succinic anhydride, maleic anhydride, pyromellitic dianhydride, acetic acid, propionic acid, butyric acid, acrylic acid, methacrylic acid, acetone, methyl ethyl ketone, benzophenone, methyl ether, ethyl ether, propyl ether, butyl ether, amyl ether. The amount of the precipitating agent is 0.03-1.0 moles, preferably 0.05-0.4 moles, per mole of magnesium halide.

The polybasic carboxylic acid ester in the above catalyst component A is selected from the group consisting of aliphatic polybasic carboxylic acid esters and aromatic polybasic carboxylic acid esters, or mixtures thereof. For example, the polybasic carboxylic acid ester can be selected from diethyl malonate, dibutyl malonate, diethyl adipate, dibutyl adipate, diethyl sebacate, dibutyl sebacate, diisobutyl phthalate, di-n-butyl phthalate, diisooctyl phthalate, diethyl maleate, di-n-butyl maleate, diethyl naphthalene dicarboxylate, dibutyl naphthalene dicarboxylate, triethyl trimellitate, tributyl trimellitate, triethyl hemimellitate, tributyl hemimellitate, tetraethyl pyromellitate, tetrabutyl pyromellitate. The amount of the polybasic carboxylic acid ester is 0.0019-0.01 moles, preferably 0.0040-0.0070 moles, per mole of magnesium halide.

The organic aluminum compound in the above catalyst component B is represented by the general formula AlR_nX_{3-n}, wherein R is hydrogen, a hydrocarbon group having 1 to 20 carbon atoms, particularly alkyl, aralkyl, aryl group; X is halogen, particularly chlorine and bromine; n is $0 < n \leq 3$. In concrete, the compound can be selected from for example, trimethyl aluminum, triethyl aluminum, triisobutyl aluminum, trioctyl aluminum, diethyl aluminum hydride, diisobutyl aluminum hydride, diethyl aluminum chloride, diisobutyl aluminum chloride, sesquiethyl aluminum chloride, and ethyl aluminum dichloride, among which triethyl aluminum and triisobutyl aluminum are preferred.

The organic silicon compound in the above catalyst component C is represented by the general formula $R_nSi(OR')_{4-n}$, wherein $0 \leq n \leq 3$, R and R' are the same or different alkyl, cycloalkyl, aryl or halogenated alkyl groups. In concrete, the

compound can be selected from, for example, trimethyl methoxysilane, trimethyl ethoxysilane, dimethyl dimethoxysilane, dimethyl diethoxysilane, methyl cyclohexyl dimethoxysilane, dibutyl dimethoxysilane, diphenyl dimethoxysilane, diphenyl diethoxy silane, phenyl trimethoxysilane and vinyl trimethoxysilane.

In the above catalyst system, the mole ratio of aluminum in the component B to titanium in the component A is 5-1000, preferably 25-300; the mole ratio of silicon in the component C to titanium in the component A is 2-100, preferably 8-32.

The method for preparing the above catalyst component A comprises the following steps:

1. Magnesium halide is dissolved with stirring in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent at a temperature of 0-100℃, preferably 30-70℃, to form a transparent homogeneous solution;

2. In the presence of a precipitating agent and at a temperature of -35-60℃, preferably -30-5℃, a titanium compound is added to the magnesium halide solution or the magnesium halide solution is added to a titanium compound, and moreover, a polybasic carboxylic acid ester needs to be added before or after the precipitation of a solid to thereby treat the precipitated solid and make the polybasic carboxylic acid ester partially loaded on the solid;

3. The reaction mixture is heated to a temperature of 60-110℃, and the suspension is stirred at this temperature for 10 minutes to 10 hours;

4. After end of the stirring, the solid is precipitated from the mixture solution, followed by filtering, removing mother liquor, and washing the solid with toluene and hexane, to obtain the solid catalyst component A comprising titanium.

The three catalyst components may be added to the polymerization reactor directly, or may be added to the reactor after being subjected to pre-complexation and/or prepolymerization. The reactor for pre-complexation reaction may be in various forms. For example, it may be a continuous stirred tank reactor, a loop reactor, a

section of pipe containing static mixer, or even a section of pipe in which the material is in a turbulent state.

The inventors have unexpectedly found that, by subjecting the selected catalyst of the present invention to a pre-complexation treatment, it is possible to obtain a propylene-butene-1 random copolymer having both a high relative dispersity of butene-1 and a low xylene solubles content at room temperature. The pre-complexation temperature can be controlled in the range of -10-60℃, preferably in the range of 0-30℃. The inventors have further found that, the relative dispersity of butene-1 in the propylene-butene-1 random copolymer of the present invention increases as the pre-complexation time prolongs, while the xylene solubles content at room temperature deceases as the pre-complexation time prolongs. However, a too long pre-complexation time will affect negatively the activity of the catalyst. Therefore, the pre-complexation time as selected in the present invention is 0.1-100 min, preferably 1-30 min.

The pre-complexed catalyst can also be optionally further subjected to prepolymerization. The prepolymerization can be carried out continuously under bulk liquid phase conditions, and can also be carried out intermittently in an inert solvent. The prepolymerisation reactor may be a continuous stirred tank, a loop reactor and the like. The prepolymerization temperature can be controlled in the range of -10-60℃, preferably in the range of 0-40℃. The multiple of prepolymerization is controlled to be 0.5 to 1000 times, preferably 1.0 to 500 times.

The polymerization reaction is carried out in a propylene liquid phase. When carrying out the liquid phase polymerization, the polymerization temperature is 0-150℃, preferably 40-100℃; the polymerization pressure should be higher than the saturated vapor pressure of propylene at the corresponding polymerization temperature.

The polymerization can be carried out continuously, and can also be carried out intermittently. The continuous polymerization can be carried out in one or more liquid

phase reactors connected in series. The liquid phase reactor can be a loop reactor, or a continuous stirred tank reactor.

Furthermore, the polymerization can also be carried out in gas phase. In this case, some suitable devices like a gas phase reactor can be employed.

The propylene-butene-1 random copolymer of the present invention can be subjected to extrusion granulation by using corresponding equipments. In the case of granulation, if required, other additives as generally used in this field, for example, antioxidants (e.g. 1010, 168), acid absorption agent (e.g. calcium stearate), light stabilizers, heat stabilizers, coloring agents, or nucleating agents capable of modifying optical properties, can be added. All of these additives can be added in their conventional amounts. During the granulation, the temperature of melt blending of materials is the one usually adopted in the processing of propylene polymer as blending temperature, which should be selected from the temperature range wherein the propylene polymer matrix can be totally molten but not decomposed, for example 180~260℃.

In a preferred embodiment, in order to prepare the preferred propylene-butene-1 random copolymer composition of the present invention, a nucleating agent can be added to polypropylene, which can reduce the size of crystal particles of polypropylene, improve the optical properties of the material, and further improve the heat resistance of the material. Preferably, the nucleating agent is Millad 3988 (manufactured by Milliken Chemical Co.), ADK NA-21 (manufactured by Asahi Denka Corp.) and Millad NX8000 (manufactured by Milliken Chemical Corp.). The most preferable nucleating agent is Millad 3988. The nucleating agent can be added in the stage of granulation. The amount of the nucleating agent is 0.1-1 parts by weight, preferably 0.2-0.4 parts by weight. The method for preparing the composition comprises melt blending the propylene-butene-1 random copolymer powder with the preferred Millad 3988 nucleating agent and optionally other additives according to the above mentioned weight ratio.

The composition of the present invention also has the following technical features: a haze of the sheet (with a thickness of 1 mm) formed by melt injection molding of less than 10%, preferably less than 8%; and a heat distortion temperature of greater than 95℃, preferably greater than 100℃, more preferably greater than 105℃. The composition of the present invention has better transparency and heat resistance, and it is more suitable for packaging food that may be edible after heating. Moreover, the composition has also a lower migrants content, so that, when used as packaging material, it can advantageously avoid the contamination of the packaged items from the precipitation of migrants, and it is especially for use as food and pharmaceutical packaging materials.

The present invention further provides a food packaging container, which is formed by the polypropylene copolymer of the present invention or the polypropylene copolymer composition as above described. The method for preparing the container comprises: melting the particles of the polypropylene composition and forming by using any molding process. The molding process may be injection molding, thermoforming, blow molding and the like. The packaging container of the present invention is suitable for packaging liquid or solid food, particularly greasy food.

MODE OF CARRYING OUT THE INVENTION

The present invention is further described by illustrating the following examples. The scope of the present invention is not limited to these examples. The scope of the present invention is defined in the claims.

The relevant data in the present invention and its examples are obtained according to the following measurement methods:

1. The measurement of the content and relative dispersity ($MD_{relative(B)}$, relative monomer dispersity) of the comonomer butene-1 in the propylene-butene-1 random copolymer:

The measurement is conducted by using AVANCE III type 400 MHz nuclear magnetic resonance spectroscopy (NMR), manufactured by Bruker Co. (Switzerland), under the following conditions and parameters: deuterated o-dichlorobenzene as solvent, 250 mg sample / 2.5 ml solvent, dissolving sample at 140℃, collecting ^{13}C-NMR, detection temperature 125℃, detection head 10 mm, delay time D1 being 10 seconds, sampling time AT being 5 seconds, scanning times > 5000 times. The operation of experiments, the identification of spectrum peaks and the data processing are conducted in accordance with the norms of standard NMR. With respect to more detailed contents, please refer to the following documents: (1) H. N. Cheng, ^{13}C NMR Analysis of Propylene-Butylene Copolymers by a Reaction Probability Model, Journal of Polymer Science: Polymer Physics Edition, 21, 573-581 (1983). (2) Eric T. Hsieh, and James C. Randall, Monomer Sequence Distributions in Ethylene-1-Hexene Copolymers, Macromolecules, 15, 1402-1406 (1982).

The relative dispersity ($MD_{relative(B)}$) of butene (B) is calculated according to the following equation:

(1) $$MD_{observed(B)} = \frac{\frac{1}{2}[PB]}{[B]} \times 100$$

(2) $$MD_{random(B)} = (1 - [B]) \times 100$$

(3) $$MD_{relative(B)} = \frac{MD_{observed(B)}}{MD_{random(B)}} \times 100$$

Wherein, [PB] represents the number of butene-1 monomeric units linked to propylene monomeric units in the molecular chain; [B] represents the total number of butene-1 monomeric units in the molecular chain; $MD_{observed(B)}$ is the dispersion coefficient of butene-1 monomers in the molecular chain, $MD_{random(B)}$ is the ideal random dispersion coefficient, $MD_{relative(B)}$ is the relative dispersity of butene-1; and $MD_{observed(B)}$, $MD_{random(B)}$ and $MD_{relative(B)}$ are calculated in unit %.

2. The xylene solubles content: measured according to ASTM D5492-98.

3. Melt index (MFR): measured according to ISO1133, at 230℃, under a load of 2.16 kg.

4. Molecular weight distribution index Mw/Mn: molecular weight distribution of sample is measured by using PL-GPC 220 gel permeation chromatographic analyzer (manufactured by Polymer Laboratories Co., British) in combination with IR5 detector (manufactured by Polychar Corp., Spain) under the following conditions and parameters: chromatographic columns – three Plgel 10 μm MIXED-B columns connected in series, solvent and mobile phase – 1,2,4-trichlorobenzene (containing 0.3 g/1000 ml antioxidant 2,6-di-butyl p-cresol), column temperature 150℃, flow rate of 1.0 ml/min, EasiCal PS-1 narrow distribution polystyrene standard sample (manufactured by PL Co.) useful for universal calibration.

5. Heat distortion temperature (HDT): measured according to ASTM D648.

6. Haze: measured according to ASTM D1003.

7. n-Hexane extract: measured according to GB/T5009.58

The above measurements are all carried out under room temperature conditions, unless otherwise indicated.

Example 1

The polymerization reaction was carried out in a pilot plant. The main equipment includes a pre-complexation reactor, a prepolymerization reactor, a loop reactor. The polymerization method and steps were as follows:

(1) Pre-complexation reaction:

The main catalyst (an active solid catalyst component comprising titanium) was obtained by using the method described in Example 1 of Chinese patent CN1258683A, wherein the internal electron donor compound was diisobutyl phthalate. The obtained main catalyst contained 1.93 wt% of Ti, 19.8 wt% of magnesium, and 9.3 wt% of diisobutyl phthalate.

The main catalyst, co-catalyst (triethylaluminum) and external electron donor (methyl cyclohexyl dimethoxysilane) were fed respectively via different pipes to a jacketed continuous stirred tank for carrying out pre-complexation reaction. The pre-complexation temperature was controlled through the jacketed water to be 8℃, and the various reaction media were charged from the bottom, and discharged via overflow. Hexane was used to dilute the cocatalyst and the external electron donor thereby controlling the volume flow of these two materials, and further controlling the residence time in the pre-complexation reactor to be 1 minute.

(2) Prepolymerization reaction:

The pre-complexed catalyst, entrained in propylene cooled to 10℃, was fed continuously to a prepolymerization reactor for carrying out prepolymerization. The prepolymerization reactor was a continuous stirred tank operated at full load. The prepolymerization was carried out in bulk liquid phase of propylene (the prepolymerization temperature and time were shown in Table 1). Under these conditions, the prepolymerized multiple of the catalyst was about 80 to 120 times.

(3) Copolymerization of propylene-butene-1:

The prepolymerized catalyst was fed to a loop reactor, wherein the copolymerization of propylene-butene-1 was accomplished. The polymerization reaction temperature was 70 ℃, and the reaction pressure was 4.0 MPa.

The amounts of butene-1 and hydrogen added in the loop reactor were shown in

Table 1.

The polymer discharged from the loop reactor was subjected to a flash evaporation to separate propylene, and then passed through wet nitrogen to eliminate the activity of unreacted catalyst, followed by drying with heating. Finally polymer powders were obtained.

To 100 parts by weight of the obtained polymer powder, 0.1 parts by weight of IRGAFOS 168 additive (Ciba Specialty Chemicals), 0.2 parts by weight of IRGANOX 1010 additive (Ciba Specialty Chemicals) and 0.05 parts by weight of calcium stearate (Ciba Specialty Chemicals) were added respectively, and then granulated with a twin screw extruder to obtain pellets of the propylene-butene-1 random copolymer. The performance of the copolymer was tested and shown in Table 1.

Example 2

The procedures were the same as Example 1, except that the pre-complexation time of the catalyst was changed. The polymerization conditions and the performance of the polymer were shown in Table 1.

Example 3

The procedures were the same as those in Example 1, except that the amount of butene-1, the amount of hydrogen and the pre-complexation time of the catalyst were changed. The polymerization conditions and the performance of the polymer were shown in Table 1.

Example 4

The procedures were the same as those in Example 1, except that the amount of butene-1 and the pre-complexation time of the catalyst were changed. The polymerization conditions and the performance of the polymer were shown in Table

1.

Comparative Example 1

The procedures were the same as those in Example 1, except that the catalyst was not subjected to pre-complexation. The main catalyst, co-catalyst (triethylaluminum) and external electron donor (methyl cyclohexyl dimethoxysilane) were fed separately to a prepolymerization reactor directly. The polymerization conditions and the performance of the polymer were shown in Table 1.

Comparative Example 2

The procedures were the same as those in Example 4, except that the catalyst was not subjected to pre-complexation. The main catalyst, co-catalyst (triethylaluminum) and external electron donor (methyl cyclohexyl dimethoxysilane) were fed separately to a prepolymerization reactor directly. The polymerization conditions and the performance of the polymer were shown in Table 1.

Comparative Example 3

The main catalyst (the solid active center component comprising titanium) was obtained by using the method described in Example 1 of Chinese patent CN200410062291.3 (including the content "Preparation of Particles of Magnesium Chloride/Alcohol Adduct" in Example 1 and "General Procedure for Preparing a Spheric Catalyst Component" before Example 1), wherein the internal electron donor compound was di-n-butyl phthalate. The obtained main catalyst contained 2.4 wt% of Ti, 18.0 wt% of magnesium, and 13 wt% of di-n-butyl phthalate.

Other operations were the same as those in Example 4. The polymerization conditions and the performance of the polymer were shown in Table 1.

120100	120100	135000	196000	120100	196000	196000
1510	1510	800	1510	1510	1510	1510
3.4	3.4	3.7	5.5	3.4	5.5	5.5
99.1	99.6	99.6	99.6	98.2	98.0	98.1
1.54	1.30	1.30	1.8	2.8	3.2	3.5
3.9	3.9	4.5	4.0	3.9	4.0	5.0
9.3	9.2	4	9.2	9.2	9.3	9.3
95	98	97	92	88	85	84
42	42	41	38	42	38	38

able 1 refers to the mass ratio of triethylaluminum to methyl cyclohexyl dimethoxysilane.

As could be seen from the above data, with respect to the selected catalyst of the present invention, the propylene-butene-1 random copolymer resulted by using the catalyst that had been subjected to pre-complexation treatment had a significant increase in the relative dispersity of butene-1 and a significant decrease in the xylene solubles content at room temperature, in comparison with the propylene-butene-1 random copolymer resulted by using the catalyst that had not been subjected to pre-complexation treatment. In the case of the same butene content, the copolymer had a similar transparency, but an increased heat distortion temperature. This demonstrated that the heat resistance of the material was improved. Moreover, as the pre-complexation time prolonged, the above effects could be further improved. As could be seen from the data of Comparative Example 3 and Example 4, the pre-complexation imposed a significant impact on the obtained performance of the selected catalyst of the present invention, that is to say, the selected catalyst of the present invention and the pre-complexation produced a synergistic effect.

Example 5 (a composition of the present invention)

The procedures of examples 1 to 4 and comparative examples 1 to 3 were repeated with the exception that 0.3 part by weight of nucleating agent Millad 3988 (Milliken Chemical Company, Ltd.), 0.1 parts by weight of IRGAFOS 168 additive (Ciba Specialty Chemicals), 0.2 parts by weight of IRGANOX 1010 additive (Ciba Specialty Chemicals) and 0.05 parts by weight of calcium stearate (Ciba Specialty Chemicals) were added respectively into each 100 parts by weight of the obtained polymer powders and then granulated by two-screw extruder, thereby obtaining the pellets of the compositions 1 to 4 (Comp. 1-4) and comparative compositions 1 to 3 (Comparative Comp. 1-3). The

performances of the compositions were shown in Table 2.

Table 2 Overview of performances of compositions

	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comparative Comp. 1	Comparative Comp. 2	Comparative Comp. 3
Heat distortion temperature, ℃	101	106	106	98	93	88	86
Haze, %	7.6	7.5	7.4	6.0	7.7	6.2	6.2
n-Hexane extract, g/100g	0.8	0.7	0.7	1.0	1.1	1.3	1.4

As could be seen from Table 2, the composition prepared from the propylene-butene-1 random copolymer having a higher relative dispersity of butene-1 and a lower xylene solubles content after the addition of a nucleating agent had better transparency and heat resistance and lower migrants content.

Example 6 (food packaging container of the present invention)

The food packaging container of the present invention was produced by an injection moulding process. In this process, the pellets of composition 1 as prepared in Example 5 were dried in a thermostatic oven at temperature of 90℃ for 4 hours. The materials were turned into a molten state in cylinder of the injection machine by the homogeneous heating. Under a certain pressure and injection rate, a defined amount of molten materials were injected into the mold cavity, subjected to a pressure keeping stage and then cooled to be solidified to a shaped article. During the whole injection moulding process the following parameters and conditions were adopted: the temperature of injection machine being

190℃ ~ 220℃, the injection pressure being 50 ~ 60 MPa, dwell pressure being 50 ~ 60 MPa, dwell time being 30 ~ 40 seconds, cooling time being 15 ~ 20 seconds and the mold temperature being 35 ~ 45℃.

Claims

1. A propylene-butene-1 random copolymer, characterized in that it has a butene-1 content of 1-6 mol%, preferably 3-6 mol%, and has a relative dispersity of butene-1, as determined according to NMR method, of greater than 98.5%, preferably greater than 99.0%.

2. The propylene-butene-1 random copolymer as claimed in claim 1, characterized in that it has a xylene solubles content at room temperature which is lower than the following fitted line: Y = 0.77 +0.252X, wherein Y is the weight percent of the xylene solubles at room temperature, and X is the mole percent of butene-1 in the propylene-butene-1 random copolymer.

3. The propylene-butene-1 random copolymer as claimed in claim 1 or 2, characterized in that it has a melt index, as measured at 230℃ under a load of 2.16 kg, of 0.5-50 g/10 min, preferably 2-30 g/10 min.

4. The propylene-butene-1 random copolymer as claimed in any one of claims 1 to 3, characterized in that it has a molecular weight distribution index Mw/Mn, as measured according to GPC, of 3.5-8, preferably 3.8-6.

5. The propylene-butene-1 random copolymer as claimed in any one of claims 1 to 4, characterized in that it is obtained by copolymerization with the use of a Ziegler-Natta catalyst comprising a main catalyst component A, a co-catalyst component B and an external electron donor component C, wherein the component A is a solid catalyst component comprising titanium and a polybasic carboxylic acid ester obtained by dissolving

magnesium halide in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent;
the component B is an alkyl aluminum compound having the general formula AlR_nX_{3-n}, wherein R is hydrogen or a hydrocarbon group having 1 to 20 carbon atoms, X is halogen; and
the component C is an organosilicon compound having the general formula $R_nSi(OR')_{4-n}$, where $0 \leq n \leq 3$, R and R' are the same or different alkyl groups, cycloalkyl groups, aryl groups or halogenated alkyl groups.

6. The propylene-butene-1 random copolymer as claimed in claim 5, characterized in that, in the solvent system, based on per mole of the magnesium halide, the amount of the organic epoxy compound is 0.2-5 moles, and the mole ratio of the organic epoxy compound to the organic phosphorus compound is 0.9-1.6.

7. The propylene-butene-1 random copolymer as claimed in claim 5 or 6, characterized in that, the mole ratio of the component B to the component A, measured as the mole ratio of aluminum to titanium, is 5-1000, and the ratio of the component C to the component A, measured as the mole ratio of silicon to titanium, is 2-100.

8. The propylene-butene-1 random copolymer as claimed in any one of claims 5 to 7, characterized in that the main catalyst component A is obtained by dissolving magnesium halide in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent to form a homogeneous solution, mixing the solution with titanium halide or a derivative thereof to precipitate a solid in the presence of a precipitating agent, treating the solid with a polybasic carboxylic acid ester to make it loaded onto the solid, and then treating the solid with titanium tetrahalide and an inert diluent, wherein the

precipitating agent is one selected from an organic acid anhydride, an organic acid, an ether and a ketone.

9. The propylene-butene-1 random copolymer as claimed in any of claims 5 to 8, characterized in that, in the homogeneous solution formed from magnesium halide useful for preparing the component A, based on per mole of magnesium halide, the amount of the organic epoxy compound is 0.6-2 moles; the mole ratio of the organic epoxy compound to the organic phosphorus compound is 0.9-1.4; the amount of the inert diluent is 1200-2400 ml.

10. The propylene-butene-1 random copolymer as claimed in any one of claims 5 to 9, characterized in that the magnesium halide useful for preparing the component A is one selected from magnesium dihalide, complexes of magnesium dihalide with water or alcohol, and derivatives obtained by replacing one halogen atom in the molecular formula of magnesium dihalide with hydrocarbon group or halohydrocarbyloxy group, or a mixture thereof.

11. The propylene-butene-1 random copolymer as claimed in any one of claims 5 to 10, characterized in that the organic epoxy compound useful for preparing the component A is one selected from ethylene oxide, propylene oxide, butylene oxide, butadiene oxide, butadiene dioxide, epichlorohydrin, methyl glycidyl ether, diglycidyl ether, tetrahydrofuran, or a mixture thereof.

12. The propylene-butene-1 random copolymer as claimed in any one of claims 5 to 11, characterized in that the organic phosphorus compound useful for preparing the component A is one selected from trimethyl ortho-phosphate, triethyl ortho-phosphate, tributyl ortho-phosphate,

triphenyl ortho-phosphate, trimethyl phosphite, triethyl phosphite, tributyl phosphite, benzyl phosphite, or a mixture thereof.

13. The propylene-butene-1 random copolymer as claimed in any one of claims 8 to 12, characterized in that the precipitating agent useful for preparing the component A is one selected from acetic anhydride, phthalic anhydride, succinic anhydride, maleic anhydride, pyromellitic dianhydride, acetic acid, propionic acid, butyric acid, acrylic acid, methacrylic acid, acetone, methyl ethyl ketone, benzophenone, methyl ether, ethyl ether, propyl ether, butyl ether, amyl ether, or a mixture thereof.

14. The propylene-butene-1 random copolymer as claimed in any one of claims 5 to 13, characterized in that the polybasic carboxylic acid ester useful for preparing the component A is one selected from diethyl malonate, dibutyl malonate, diethyl adipate, dibutyl adipate, diethyl sebacate, dibutyl sebacate, diisobutyl phthalate, di-n-butyl phthalate, diisooctyl phthalate, diethyl maleate, di-n-butyl maleate, diethyl naphthalene dicarboxylate, dibutyl naphthalene dicarboxylate, triethyl trimellitate, tributyl trimellitate, triethyl hemimellitate, tributyl hemimellitate, tetraethyl pyromellitate, tetrabutyl pyromellitate.

15. The propylene-butene-1 random copolymer as claimed in any one of claims 8 to 14, characterized in that the titanium halide or its derivative useful for preprating the component A is one selected from titanium tetrachloride, titanium tetrabromide, titanium tetraiodide, tetrabutoxy titanium, tetraethoxy titanium, monochloro triethoxy titanium, dichloro diethoxy titanium, trichloro monoethoxy titanium, or a mixture thereof.

16. The propylene-butene-1 random copolymer as claimed in any one of

claims 5 to 15, characterized in that the method for preparing the catalyst component A comprises the following steps:

1). Magnesium halide is dissolved with stirring in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent at a temperature of 0-100℃ to form a transparent homogeneous solution;

2). In the presence of a precipitating agent and at a temperature of -35-60℃, a titanium compound is added to the magnesium halide solution or the magnesium halide solution is added to a titanium compound, and moreover, a polybasic carboxylic acid ester needs to be added before or after the precipitation of a solid to thereby treat the precipitated solid and make the polybasic carboxylic acid ester partially loaded on the solid;

3). The reaction mixture is heated to a temperature of 60-110℃, and the suspension is stirred at this temperature for 10 minutes to 10 hours;

4). After end of the stirring, the solid is precipitated from the mixture solution, followed by filtering, removing mother liquor, and washing the solid with toluene and hexane, to obtain the solid catalyst component A comprising titanium.

17. The propylene-butene-1 random copolymer as claimed in any one of claims 5 to 16, characterized in that the three catalyst components A, B and C are subjected to pre-complexation and optional prepolymerization and then added to the reactor.

18. The propylene-butene-1 random copolymer as claimed in claim 17, characterized in that the pre-complexation temperature is controlled in the range of -10-60℃, preferably in the range of 0-30℃.

19. The propylene-butene-1 random copolymer as claimed in claim 17 or 18, characterized in that the pre-complexation time is 0.1-100 min, preferably 1-30 min.

20. The propylene-butene-1 random copolymer as claimed in any one of claims 5 to 19, characterized in that the copolymerization of propylene and butene-1 is carried out in a liquid phase loop reactor.

21. A method for preparing a propylene-butene-1 random copolymer according to any one of claims 1 to 20, characterized in that propylene and butene-1 are copolymerized by adjusting the amount of the comonomer butene-1 added in the reactor, in the presence of a Ziegler-Natta catalyst comprising a main catalyst component A, a co-catalyst component B and an external electron donor component C, at a polymerization temperature and with an appropriate hydrogen content,

wherein the component A is a solid catalyst component comprising titanium and a polybasic carboxylic acid ester obtained by dissolving magnesium halide in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent;

the component B is an alkyl aluminum compound having the general formula AlR_nX_{3-n}, wherein R is hydrogen or a hydrocarbon group having 1 to 20 carbon atoms and X is halogen; and

the component C is an organosilicon compound having the general formula $R_nSi(OR')_{4-n}$, where $0 \leq n \leq 3$, R and R' are the same or different alkyl groups, cycloalkyl groups, aryl groups or halogenated alkyl groups.

22. The method according to claim 21, wherein the three catalyst components A, B and C are subjected to pre-complexation and optional

prepolymerization and then added to the reactor.

23. A propylene-butene-1 random copolymer composition, which comprises the propylene-butene-1 random copolymer as claimed in any one of claims 1-20 and 0.1-1 parts by weight, preferably 0.2-0.4 parts by weight, of a nucleating agent, in relative to 100 parts by weight of the propylene-butene-1 random copolymer.

24. The propylene-butene-1 random copolymer composition as claimed in claim 23, characterized in that the nucleating agent is Millad 3988 nucleating agent, ADK NA-21 nucleating agent and Millad NX8000 nucleating agent.

25. The propylene-butene-1 random copolymer composition as claimed in claim 23 or 24, characterized in that a sheet with a thickness of 1 mm formed from the composition by melt injection molding has a haze of less than 10%, preferably less than 8%.

26. The propylene-butene-1 random copolymer composition as claimed in any one of claims 23 to 25, characterized in that the composition has heat distortion temperature of greater than 95℃, preferably greater than 100℃, more preferably greater than 105℃.

27. A method for preparing the propylene-butene-1 random copolymer composition as claimed in any one of claims 23 to 26, which comprises the step of melt blending the propylene-butene-1 random copolymer powder with a nucleating agent and optionally other additives.

28. A food packaging container, which is formed by the

propylene-butene-1 random copolymer as claimed in any one of claims 1-20 or the propylene-butene-1 random copolymer composition as claimed in any one of claims 23-27.

Propylene random copolymer, method for its preparation, and compositions and articles containing the same

Technical Field

The present invention relates to a propylene random copolymer, a method for its preparation, and compositions and articles containing the same, wherein the propylene random copolymer is particularly a propylene-butene-1 random copolymer.

Background Art

Propylene random copolymer usually refers to a polymer obtained by randomly copolymerizing a small amount, usually not more than 15% by weight, of α-olefin monomer, for example, commonly used ethylene or butene-1, onto a polypropylene molecular chain.

For example, WO95/14738 discloses a polymer composition having improved balanced mechanical and optical properties comprising (1) a random copolymer comprising from about 8% to about 20% by weight of butene-1 and from about 80% to about 99.2% by weight of propylene, and (2) from about 0%-0.35% by weight of polymer composition of a synthetic amorphous silica antiblock agent. On the other hand, US2005/0085609 discloses a random copolymer comprising propylene and 1-butene whose content of comonomers is in the range from 0.7 to 3.0 % by weight and whose cold-xylene-soluble fraction is from 0.75 to 2.0% by weight. The copolymer is prepared in the presence of a Ziegler-Natta catalyst system. US2005/0187367 relates to a biaxially oriented film made of a thermoplastic material containing a propylene-1-butene copolymer which may comprise 3.0wt% 1-butene and have xylene soluble content below 0.7% and melt flow rate of 2.4-2.7 g/10min. The polymer is prepared using a solid catalyst made from tetrabutoxytitanium, diisobutyl phthalate and butylmagnesium chloride in combination with triethylaluminum and t-butyl-n-propyldimethoxysilane, whereas in US2002/0107351

a film comprising a propylene-1-butene random copolymer comprising preferably 3.0-8.0% by weight of 1-butene with a melt flow rate of 1.0 to 20 g/10min is formed.

Sacchi,M.C et al, "Effect of internal and external Lewis bases on propene/1-butene copolymerization with $MgCl_2$ studies the effect of internal and external Lewis bases on propene/1-butene copolymerization with $MgCl_2$-supported Ziegler-Natta catalysts, MACROMOL.CHEM.RAPID COMMUN Vol 14 Pages 231-238 (1993) studies the effect of internal and external Lewis bases on propene/1-butene copolymerization with $MgCl_2$-supported Ziegler-Natta catalysts, and especially discloses a propylene-1-butene copolymer comprising 5.7 mol% of 1-butene produced by a catalyst system with a catalyst made from $MgCl_2$, diisobutyl phthalate and $TiCl_4$ together with $Al(C_2H_5)_3$ and $C_6H_5(C_2H_5O)_3Si$.

Other patent prior art for example WO97/31954 discloses a random copolymer of propylene and 1-butene made with the use of a catalyst comprising magnesium, titanium and diisobutyl phthalate in combination with triethylaluminium (TEAL) and dicyclopentyldimethoxysilane as external electron-donor compound whereas WO2010/057841 discloses a propylene copolymer comprising 1-butene as a comonomer in the range of 1.0 to 3.0 wt% and having a xylene cold soluble fraction (XCS) equal or below 2.5 wt%. The polymers are prepared using a metallocene catalyst.

Since the comonomers destroy the regularity of the arrangement of the propylene units in the molecular chain, the melting point and the degree of crystallinity of the polypropylene resin are declined. The relatively low melting point enables the polypropylene resin to be used for manufacturing a more readily heat-sealable film, while the relatively low degree of crystallinity results in improved transparency of the material. Although comonomers are often copolymerized in a larger amount in order to achieve higher transparency, the excessively increasing in the amount of comonomers may unduly reduce the degree of crystallinity of the material, thereby reducing the rigidity and heat resistance of the material, and more important also increase the content of the non-crystalline components (the soluble contents) in the

material, so that they tend to migrate onto the surface of articles and thus affect negatively the processing and application of the product. In particular, in case that the product is used for packaging greasy foods, a part of the non-crystalline components may gradually migrate to the food, and contaminate it. In addition, reducing the melting point and the degree of crystallinity usually also render heat resistance of the material deteriorated. If such a material is used in food containers, the deteriorated heat resistance makes it disadvantageous to the microwave heating. The use of comonomers in a unduly larger amount may also bring difficulties to the polymerization process, for example, the occurrence of kettle-sticking, caking and hard removal of residual monomers, in particular when the conomomer is butene-1 having higher boiling point or α-olefins having more carbon atoms.

In the prior art, butene-1 and propylene are often used to carry out random copolymerization, with the expectation that the resultant propylene-butene-1 random copolymer has a relatively low migrants content. However, the random copolymer still has drawbacks in giving consideration to both transparency and heat resistance. An existing solution is to combine with an appropriate amount of nucleating agent that can improve the transparency. Although this can, to some extent, improve the transparency and heat resistance of the copolymer material, the result is still not satisfactory in terms of the heat resistance and the migrants content.

Contents OF THE INVENTION

Therefore, one object of the present invention is to provide a propylene-butene-1 random copolymer, which is featured with good heat resistance and low xylene soluble content at room temperature, while maintaining or even further improving the excellent transparency.

The present invention is described in the claims.

By experiments, the present inventors have surprisingly found that, by increasing the relative dispersity of butene-1, the material can achieve at least the same

transparency, but better heat resistance.

In the process of randomly copolymerizing butene-1 as a comonomer with propylene, if a higher proportion of butene-1 monomers is inserted into the polypropylene molecular chain as discretely arranged monomer units, and a lower proportion of butene-1 monomers is inserted into the polypropylene molecular chain as consecutively arranged monomer units (such as BB dual units or more consecutive monomer units), the ratio of the observed dispersion coefficient $MD_{observed(B)}$ of butene-1 unit in the molecular chain to the ideal random dispersion coefficient $MD_{random(B)}$ will be greater. This ratio is defined as the relative dispersity $MD_{relative(B)}$ of butene-1, which is calculated according to the following equation:

(1) $$MD_{observed(B)} = \frac{\frac{1}{2}[PB]}{[B]} \times 100$$

(2) $$MD_{random(B)} = (1 - [B]) \times 100$$

(3) $$MD_{relative(B)} = \frac{MD_{observed(B)}}{MD_{random(B)}} \times 100$$

Wherein, [PB] represents the number of butene-1 monomeric units linked to propylene monomeric units in the molecular chain; [B] represents the total number of butene-1 monomeric units in the molecular chain; and $MD_{observed(B)}$, $MD_{random(B)}$ and $MD_{relative(B)}$ are calculated in unit %.

Another object of the present invention is to provide a method for preparing propylene-butene-1 random copolymer. The method is capable of preparing propylene-butene-1 random copolymer with a very high relative dispersity of butene-1 and a low xylene soluble content at room temperature. Moreover, the polymerization process is easy to operate, and can avoid the occurrence of kettle-sticking, caking and hard removal of residual monomers.

Still another object of the present invention is to provide a polypropylene composition, in particular a propylene-butene-1 random copolymer composition, which has high transparency, low migrants content and high heat resistance.

Still another object of the present invention is to provide a food packaging container, which has high transparency, low migrants content and high heat resistance.

In addition, the present invention also provides methods for preparing the polypropylene composition and the food packaging container as described above.

The propylene-butene-1 random copolymer in the present invention has a butene-1 content of 1-6 mol%, preferably 3-6 mol%, and has a relative dispersity of butene-1, as determined according to NMR method, of greater than 98.5%, preferably greater than 99.0%.

The butene-1 content in the propylene-butene-1 random copolymer may affect the degree of crystallinity of polypropylene. The higher the butene-1 content is, the lower the degree of crystallinity of polypropylene will be, and the better the transparency of the material will be. However, an excessively high butene-1 content may result in excessive xylene solubles at room temperature, while an excessively low butene-1 content may result in a excessively high degree of crystallinity which influences the transparency. By a large number of experiments, it has been found that the butene-1 content is preferably 1-6 mol%, more preferably 3-6 mol%.

As mentioned above, by increasing the relative dispersity of butene-1 in the propylene-butene-1 random copolymer, the material may have better heat resistance while achieving the same transparency. The relative dispersity of butene-1 in the propylene-butene-1 random copolymer of the present invention can be up to greater than 98.5%, preferably greater than 99.0%.

Due to a very high relative dispersity of butene-1, the propylene-butene-1 random copolymer of the present invention can have a heat distortion temperature up to

above 90□, preferably above 95□.

The increase of the amount of comonomer in propylene random copolymer may usually lead to the increase of the xylene solubles content at room temperature, and such a result applies also to butene-1 as a comonomer. In general, a relatively high xylene solubles content at room temperature may result that the product as a packaging material is not allowed to be in direct contact with food, or pharmaceuticals, or else, it may contaminate the packaged items. However, within the butene-1 content range in the propylene-butene-1 random copolymer as suggested in the present invention, the xylene solubles content at room temperature increases slowly as the butene-1 content increases.

In concrete, the xylene solubles content at room temperature (about 25□) in the propylene-butene-1 random copolymer of the present invention is lower than the following fitted line:

$Y = 0.77 + 0.252X$

Wherein: Y is the weight percent of xylene solubles at room temperature (e.g. in case of 5 wt%, Y = 5); X is the mole percent of butene-1 in the propylene-butene-1 random copolymer (e.g. in case of 5 mol%, X = 5).

Due to the reduction in the xylene solubles content at room temperature, the propylene-butene-1 random copolymer of the present invention, when used for food packaging containers, has higher food safety; and, when used for film processing, it is not easy to stick rollers and makes the metal plating layer not so easy to be detached.

Usually, the processability of the polymer is controlled by controlling the melt index. Preferably, the propylene-butene-1 random copolymer of the present invention has a melt index, as measured at 230℃ under a load of 2.16 kg, of 0.5-50 g/10 min, preferably 2-30 g/10 min.

The propylene-butene-1 random copolymer of the present invention has a molecular weight distribution index Mw/Mn for characterizing the molecular weight distribution, as measured according to GPC, of 3.5-8, preferably 3.8-6. A too small molecular weight distribution index means that the molecular weight distribution is narrow, so that the processing performance of the material becomes poor; and a too large molecular weight distribution index means that the molecular weight distribution is wide, so that the transparency of the material may be affected and reduced.

The propylene-butene-1 random copolymer of the present invention having a high relative dispersity of butene-1 in combination with better transparency and heat resistance is very suitable for packaging food that may be edible after heating. Moreover, the copolymer has such a lower xylene solubles content at room temperature that, when used as packaging material, it can advantageously avoid the contamination of the packaged items from the precipitation of room temperature solubles, and may be more suitable for using as food and pharmaceutical packaging materials.

The method for preparing the propylene-butene-1 random copolymer of the present invention comprises: the copolymerization of propylene and butene-1 is carried out by adjusting the amount of the comonomer butene-1 added in the reactor to obtain the propylene-butene-1 random copolymer in the presence of a selected Ziegler-Natta catalyst and at a polymerization temperature and an appropriate hydrogen content.

The selected Ziegler-Natta catalyst in the present invention refers to the catalysts as described in Chinese Patents CN85100997A, CN1258680A, CN1258683A, CN1258684A. The catalyst as described in Chinese patent CN1258683A particularly has advantages when used as the catalyst of the present invention.

In a specific embodiment, the propylene-butene-1 random copolymer is obtained by copolymerization with the use of a Ziegler-Natta catalyst comprising a main catalyst component A, a co-catalyst component B and an external electron donor component

C,

wherein the main catalyst component A is a solid catalyst component comprising titanium and a polybasic carboxylic acid ester obtained by dissolving magnesium halide in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent;

the component B is an alkyl aluminum compound having the general formula AlR_nX_{3-n}, wherein R is hydrogen or a hydrocarbon group having 1 to 20 carbon atoms, X is halogen; and

the component C is an organosilicon compound having the general formula $R_nSi(OR')_{4-n}$, where $0 \leq n \leq 3$, R and R' are the same or different alkyl groups, cycloalkyl groups, aryl groups or halogenated alkyl groups.

Preferably, in the solvent system as described above, based on per mole of the magnesium halide, the amount of the organic epoxy compound is 0.2-5 moles, and the mole ratio of the organic epoxy compound to the organic phosphorus compound is 0.9-1.6.

Preferably, the mole ratio of the component B to the component A, measured as the mole ratio of aluminum to titanium, is 5-1000, and the ratio of the component C to the component A, measured as the mole ratio of silicon to titanium, is 2-100.

The main catalyst component A may be, for example, obtained by dissolving magnesium halide in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent to form a homogeneous solution, then mixing the solution with titanium halide or a derivative thereof to precipitate a solid in the presence of a precipitating agent, treating the solid with a polybasic carboxylic acid ester to make it loaded on the solid, and then treating the solid with titanium tetrahalide and an inert diluent, wherein the precipitating agent is one selected from an organic acid anhydride, an organic acid, an ether and a ketone.

The further preferred Ziegler-Natta catalyst in the present invention is characterized

in that it comprises a main catalyst component A, a co-catalyst component B and an external electron donor component C,

wherein the component A is a solid catalyst component comprising titanium, obtained by dissolving magnesium halide in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent to form a homogeneous solution, mixing the solution with titanium halide or a derivative thereof to precipitate a solid in the presence of a precipitating agent, treating the solid with a polybasic carboxylic acid ester to make it loaded on the solid, and then treating the solid with titanium tetrahalide and an inert diluent, wherein the precipitating agent is one selected from an organic acid anhydride, an organic acid, an ether and a ketone and in the solvent system as described above, based on per mole of the magnesium halide, the amount of the organic epoxy compound is 0.2-5 moles, and the mole ratio of the organic epoxy compound to the organic phosphorus compound is 0.5-1.6;

the component B is an alkyl aluminum compound having the general formula AlR_nX_{3-n}, where R is hydrogen or a hydrocarbon group having 1 to 20 carbon atoms, X is halogen; and

the component C is an organosilicon compound having the general formula $R_nSi(OR')_{4-n}$, where $0 \leq n \leq 3$, R and R' are the same or different alkyl groups, cycloalkyl groups, aryl groups or halogenated alkyl groups;

the mole ratio of the component B to the component A, measured as the mole ratio of aluminum to titanium, is 5-1000, and the ratio of the component C to the component A, measured as the mole ratio of silicon to titanium, is 2-100.

The magnesium halide in the above catalyst component A includes magnesium dihalide, complexes of magnesium dihalide with water, or alcohol, and derivatives obtained by replacing one halogen atom in the molecular formula of magnesium dihalide with hydrocarbon group or halohydrocarbyloxy group. With respect to the magnesium dihalide as mentioned above, it can be magnesium dichloride, magnesium dibromide and magnesium diiodide.

The organic epoxy compound in the above catalyst component A includes aliphatic

olefins having 2 to 8 carbon atoms, diolefins or halogenated aliphatic olefins or oxides of diolefins, glycidyl ethers, and inner ethers. As the concrete examples for the above list, the useful compound can be selected from ethylene oxide, propylene oxide, butylene oxide, butadiene oxide, butadiene dioxide, epichlorohydrin, methyl glycidyl ether, diglycidyl ether, tetrahydrofuran.

The organic phosphorus compound in the above catalyst component A includes hydrocarbyl esters or halogenated hydrocarbyl esters of ortho-phosphoric acid or phosphorous acid. In concrete, such a compound can be, for example, trimethyl ortho-phosphate, triethyl ortho-phosphate, tributyl ortho-phosphate, triphenyl ortho-phosphate, trimethyl phosphite, triethyl phosphite, tributyl phosphite, benzyl phosphite.

The inert diluent in the above catalyst component A may include hexane, heptane, octane, benzene, toluene, xylene, 1,2-dichloroethane, chlorobenzene and other hydrocarbon or halogenated hydrocarbon compounds.

The magnesium halide solution in the above catalyst component A has the following composition: based on per mole of magnesium halide, the amount of the organic epoxy compound is 0.2-5 moles, preferably 0.5-2 moles; the mole ratio of the organic epoxy compound to the organic phosphorus compound is 0.5-1.6, preferably 0.9-1.6, most preferably 0.9-1.4; and the amount of the inert diluent is 1200-2400 ml, preferably 1400-2000 ml.

The halide of transition metal Ti or its derivative in the above catalyst component A is represented by the general formula $TiX_n(OR)_{4-n}$, where n = 1-4. In concrete, the examples of such compounds may be titanium tetrachloride, titanium tetrabromide, titanium tetraiodide, tetrabutoxy titanium, tetraethoxy titanium, monochloro triethoxy titanium, dichloro diethoxy titanium, and trichloro monoethoxy titanium. The amount of the halide of transition metal Ti or its derivative is 0.5-150 moles, preferably 1-20 moles, per mole of magnesium halide.

The precipitating agent in the above catalyst component A is selected from the group consisting of organic acids, organic acid anhydrides, organic ethers, organic ketones, or mixtures thereof. As examples for the above list, the precipitating agent can be selected from acetic anhydride, phthalic anhydride, succinic anhydride, maleic anhydride, pyromellitic dianhydride, acetic acid, propionic acid, butyric acid, acrylic acid, methacrylic acid, acetone, methyl ethyl ketone, benzophenone, methyl ether, ethyl ether, propyl ether, butyl ether, amyl ether. The amount of the precipitating agent is 0.03-1.0 moles, preferably 0.05-0.4 moles, per mole of magnesium halide.

The polybasic carboxylic acid ester in the above catalyst component A is selected from the group consisting of aliphatic polybasic carboxylic acid esters and aromatic polybasic carboxylic acid esters, or mixtures thereof. For example, the polybasic carboxylic acid ester can be selected from diethyl malonate, dibutyl malonate, diethyl adipate, dibutyl adipate, diethyl sebacate, dibutyl sebacate, diisobutyl phthalate, di-n-butyl phthalate, diisooctyl phthalate, diethyl maleate, di-n-butyl maleate, diethyl naphthalene dicarboxylate, dibutyl naphthalene dicarboxylate, triethyl trimellitate, tributyl trimellitate, triethyl hemimellitate, tributyl hemimellitate, tetraethyl pyromellitate, tetrabutyl pyromellitate. The amount of the polybasic carboxylic acid ester is 0.0019-0.01 moles, preferably 0.0040-0.0070 moles, per mole of magnesium halide.

The organic aluminum compound in the above catalyst component B is represented by the general formula AlR_nX_{3-n}, wherein R is hydrogen, a hydrocarbon group having 1 to 20 carbon atoms, particularly alkyl, aralkyl, aryl group; X is halogen, particularly chlorine and bromine; n is $0 < n \leq 3$. In concrete, the compound can be selected from for example, trimethyl aluminum, triethyl aluminum, triisobutyl aluminum, trioctyl aluminum, diethyl aluminum hydride, diisobutyl aluminum hydride, diethyl aluminum chloride, diisobutyl aluminum chloride, sesquiethyl aluminum chloride, and ethyl aluminum dichloride, among which triethyl aluminum and triisobutyl aluminum are preferred.

The organic silicon compound in the above catalyst component C is represented by the general formula $R_nSi(OR')_{4-n}$, wherein $0 \leq n \leq 3$, R and R' are the same or different alkyl, cycloalkyl, aryl or halogenated alkyl groups. In concrete, the compound can be selected from, for example, trimethyl methoxysilane, trimethyl ethoxysilane, dimethyl dimethoxysilane, dimethyl diethoxysilane, methyl cyclohexyl dimethoxysilane, dibutyl dimethoxysilane, diphenyl dimethoxysilane, diphenyl diethoxy silane, phenyl trimethoxysilane and vinyl trimethoxysilane.

In the above catalyst system, the mole ratio of aluminum in the component B to titanium in the component A is 5-1000, preferably 25-300; the mole ratio of silicon in the component C to titanium in the component A is 2-100, preferably 8-32.

The method for preparing the above catalyst component A comprises the following steps:

1. Magnesium halide is dissolved with stirring in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent at a temperature of 0-100℃, preferably 30-70℃, to form a transparent homogeneous solution;

2. In the presence of a precipitating agent and at a temperature of -35-60℃, preferably -30-5℃, a titanium compound is added to the magnesium halide solution or the magnesium halide solution is added to a titanium compound, and moreover, a polybasic carboxylic acid ester needs to be added before or after the precipitation of a solid to thereby treat the precipitated solid and make the polybasic carboxylic acid ester partially loaded on the solid;

3. The reaction mixture is heated to a temperature of 60-110℃, and the suspension is stirred at this temperature for 10 minutes to 10 hours;

4. After end of the stirring, the solid is precipitated from the mixture solution, followed by filtering, removing mother liquor, and washing the solid with toluene and hexane, to obtain the solid catalyst component A comprising titanium.

The three catalyst components may be added to the polymerization reactor directly,

or may be added to the reactor after being subjected to pre-complexation and/or prepolymerization. The reactor for pre-complexation reaction may be in various forms. For example, it may be a continuous stirred tank reactor, a loop reactor, a section of pipe containing static mixer, or even a section of pipe in which the material is in a turbulent state.

The inventors have unexpectedly found that, by subjecting the selected catalyst of the present invention to a pre-complexation treatment, it is possible to obtain a propylene-butene-1 random copolymer having both a high relative dispersity of butene-1 and a low xylene solubles content at room temperature. The pre-complexation temperature can be controlled in the range of -10-60□, preferably in the range of 0-30□. The inventors have further found that, the relative dispersity of butene-1 in the propylene-butene-1 random copolymer of the present invention increases as the pre-complexation time prolongs, while the xylene solubles content at room temperature deceases as the pre-complexation time prolongs. However, a too long pre-complexation time will affect negatively the activity of the catalyst. Therefore, the pre-complexation time as selected in the present invention is 0.1-100 min, preferably 1-30 min.

The pre-complexed catalyst can also be optionally further subjected to prepolymerization. The prepolymerization can be carried out continuously under bulk liquid phase conditions, and can also be carried out intermittently in an inert solvent. The prepolymerisation reactor may be a continuous stirred tank, or a loop reactor. The prepolymerization temperature can be controlled in the range of -10-60□, preferably in the range of 0-40□. The multiple of prepolymerization is controlled to be 0.5 to 1000 times, preferably 1.0 to 500 times.

The polymerization reaction is carried out in a propylene liquid phase. When carrying out the liquid phase polymerization, the polymerization temperature is 0-150℃, preferably 40-100℃; the polymerization pressure should be higher than the saturated vapor pressure of propylene at the corresponding polymerization temperature.

The polymerization can be carried out continuously, and can also be carried out intermittently. The continuous polymerization can be carried out in one or more liquid phase reactors connected in series. The liquid phase reactor can be a loop reactor, or a continuous stirred tank reactor.

Furthermore, the polymerization can also be carried out in gas phase. In this case, some suitable devices like a gas phase reactor can be employed.

The propylene-butene-1 random copolymer of the present invention can be subjected to extrusion granulation by using corresponding equipments. In the case of granulation, if required, other additives as generally used in this field, for example, antioxidants (e.g. 1010, 168), acid absorption agent (e.g. calcium stearate), light stabilizers, heat stabilizers, coloring agents, or nucleating agents capable of modifying optical properties, can be added. All of these additives can be added in their conventional amounts. During the granulation, the temperature of melt blending of materials is the one usually adopted in the processing of propylene polymer as blending temperature, which should be selected from the temperature range wherein the propylene polymer matrix can be totally molten but not decomposed, for example 180～260℃.

In a preferred embodiment, in order to prepare the preferred propylene-butene-1 random copolymer composition of the present invention, a nucleating agent can be added to polypropylene, which can reduce the size of crystal particles of polypropylene, improve the optical properties of the material, and further improve the heat resistance of the material. Preferably, the nucleating agent is Millad 3988 (manufactured by Milliken Chemical Co.), ADK NA-21 (manufactured by Asahi Denka Corp.) and Millad NX8000 (manufactured by Milliken Chemical Corp.). The most preferable nucleating agent is Millad 3988. The nucleating agent can be added in the stage of granulation. The amount of the nucleating agent is 0.1-1 parts by weight, preferably 0.2-0.4 parts by weight. The method for preparing the composition comprises melt blending the propylene-butene-1 random copolymer powder with the

preferred Millad 3988 nucleating agent and optionally other additives according to the above mentioned weight ratio.

The composition of the present invention also has the following technical features: a haze of the sheet (with a thickness of 1 mm) formed by melt injection molding of less than 10%, preferably less than 8%; and a heat distortion temperature of greater than 95℃, preferably greater than 100℃, more preferably greater than 105℃. The composition of the present invention has better transparency and heat resistance, and it is more suitable for packaging food that may be edible after heating. Moreover, the composition has also a lower migrants content, so that, when used as packaging material, it can advantageously avoid the contamination of the packaged items from the precipitation of migrants, and it is especially for use as food and pharmaceutical packaging materials.

The present invention further provides a food packaging container, which is formed by the polypropylene copolymer of the present invention or the polypropylene copolymer composition as above described. The method for preparing the container comprises: melting the particles of the polypropylene composition and forming by using any molding process. The molding process may be injection molding, thermoforming, or blow molding. The packaging container of the present invention is suitable for packaging liquid or solid food, particularly greasy food.

MODE OF CARRYING OUT THE INVENTION

The present invention is further described by illustrating the following examples. The scope of the present invention is not limited to these examples. The scope of the present invention is defined in the claims.

The relevant data in the present invention and its examples are obtained according to the following measurement methods:

1. The measurement of the content and relative dispersity ($MD_{relative(B)}$, relative

monomer dispersity) of the comonomer butene-1 in the propylene-butene-1 random copolymer:

The measurement is conducted by using AVANCE III type 400 MHz nuclear magnetic resonance spectroscopy (NMR), manufactured by Bruker Co. (Switzerland), under the following conditions and parameters: deuterated o-dichlorobenzene as solvent, 250 mg sample / 2.5 ml solvent, dissolving sample at 140℃, collecting ^{13}C-NMR, detection temperature 125℃, detection head 10 mm, delay time D1 being 10 seconds, sampling time AT being 5 seconds, scanning times > 5000 times. The operation of experiments, the identification of spectrum peaks and the data processing are conducted in accordance with the norms of standard NMR. With respect to more detailed contents, please refer to the following documents: (1) H. N. Cheng, ^{13}C NMR Analysis of Propylene-Butylene Copolymers by a Reaction Probability Model, Journal of Polymer Science: Polymer Physics Edition, 21, 573-581 (1983). (2) Eric T. Hsieh, and James C. Randall, Monomer Sequence Distributions in Ethylene-1-Hexene Copolymers, Macromolecules, 15, 1402-1406 (1982).

The relative dispersity ($MD_{relative(B)}$) of butene (B) is calculated according to the following equation:

(1) $$MD_{observed(B)} = \frac{\frac{1}{2}[PB]}{[B]} \times 100$$

(2) $$MD_{random(B)} = (1 - [B]) \times 100$$

(3) $$MD_{relative(B)} = \frac{MD_{observed(B)}}{MD_{random(B)}} \times 100$$

Wherein, [PB] represents the number of butene-1 monomeric units linked to propylene monomeric units in the molecular chain; [B] represents the total number of butene-1 monomeric units in the molecular chain; $MD_{observed(B)}$ is the dispersion

coefficient of butene-1 monomers in the molecular chain, $MD_{random(B)}$ is the ideal random dispersion coefficient, $MD_{relative(B)}$ is the relative dispersity of butene-1; and $MD_{observed(B)}$, $MD_{random(B)}$ and $MD_{relative(B)}$ are calculated in unit %.

2. The xylene solubles content: measured according to ASTM D5492-98.

3. Melt index (MFR): measured according to ISO1133, at 230℃, under a load of 2.16 kg.

4. Molecular weight distribution index Mw/Mn: molecular weight distribution of sample is measured by using PL-GPC 220 gel permeation chromatographic analyzer (manufactured by Polymer Laboratories Co., British) in combination with IR5 detector (manufactured by Polychar Corp., Spain) under the following conditions and parameters: chromatographic columns – three Plgel 10 μm MIXED-B columns connected in series, solvent and mobile phase – 1,2,4-trichlorobenzene (containing 0.3 g/1000 ml antioxidant 2,6-di-butyl p-cresol), column temperature 150℃, flow rate of 1.0 ml/min, EasiCal PS-1 narrow distribution polystyrene standard sample (manufactured by PL Co.) useful for universal calibration.

5. Heat distortion temperature (HDT): measured according to ASTM D648.

6. Haze: measured according to ASTM D1003.

7. n-Hexane extract: measured according to GB/T5009.58

The above measurements are all carried out under room temperature conditions, unless otherwise indicated.

Example 1

The polymerization reaction was carried out in a pilot plant. The main equipment includes a pre-complexation reactor, a prepolymerization reactor, a loop reactor. The

polymerization method and steps were as follows:

(1) Pre-complexation reaction:

The main catalyst (an active solid catalyst component comprising titanium) was obtained by using the method described in Example 1 of Chinese patent CN1258683A, wherein the internal electron donor compound was diisobutyl phthalate. The obtained main catalyst contained 1.93 wt% of Ti, 19.8 wt% of magnesium, and 9.3 wt% of diisobutyl phthalate.

The main catalyst, co-catalyst (triethylaluminum) and external electron donor (methyl cyclohexyl dimethoxysilane) were fed respectively via different pipes to a jacketed continuous stirred tank for carrying out pre-complexation reaction. The pre-complexation temperature was controlled through the jacketed water to be 8□, and the various reaction media were charged from the bottom, and discharged via overflow. Hexane was used to dilute the cocatalyst and the external electron donor thereby controlling the volume flow of these two materials, and further controlling the residence time in the pre-complexation reactor to be 1 minute.

(2) Prepolymerization reaction:

The pre-complexed catalyst, entrained in propylene cooled to 10℃, was fed continuously to a prepolymerization reactor for carrying out prepolymerization. The prepolymerization reactor was a continuous stirred tank operated at full load. The prepolymerization was carried out in bulk liquid phase of propylene (the prepolymerization temperature and time were shown in Table 1). Under these conditions, the prepolymerized multiple of the catalyst was about 80 to 120 times.

(3) Copolymerization of propylene-butene-1:

The prepolymerized catalyst was fed to a loop reactor, wherein the copolymerization of propylene-butene-1 was accomplished. The polymerization reaction temperature

was 70 ℃, and the reaction pressure was 4.0 MPa.

The amounts of butene-1 and hydrogen added in the loop reactor were shown in Table 1.

The polymer discharged from the loop reactor was subjected to a flash evaporation to separate propylene, and then passed through wet nitrogen to eliminate the activity of unreacted catalyst, followed by drying with heating. Finally polymer powders were obtained.

To 100 parts by weight of the obtained polymer powder, 0.1 parts by weight of IRGAFOS 168 additive (Ciba Specialty Chemicals), 0.2 parts by weight of IRGANOX 1010 additive (Ciba Specialty Chemicals) and 0.05 parts by weight of calcium stearate (Ciba Specialty Chemicals) were added respectively, and then granulated with a twin screw extruder to obtain pellets of the propylene-butene-1 random copolymer. The performance of the copolymer was tested and shown in Table 1.

Example 2

The procedures were the same as Example 1, except that the pre-complexation time of the catalyst was changed. The polymerization conditions and the performance of the polymer were shown in Table 1.

Example 3

The procedures were the same as those in Example 1, except that the amount of butene-1, the amount of hydrogen and the pre-complexation time of the catalyst were changed. The polymerization conditions and the performance of the polymer were shown in Table 1.

Example 4

The procedures were the same as those in Example 1, except that the amount of butene-1 and the pre-complexation time of the catalyst were changed. The polymerization conditions and the performance of the polymer were shown in Table 1.

Comparative Example 1

The procedures were the same as those in Example 1, except that the catalyst was not subjected to pre-complexation. The main catalyst, co-catalyst (triethylaluminum) and external electron donor (methyl cyclohexyl dimethoxysilane) were fed separately to a prepolymerization reactor directly. The polymerization conditions and the performance of the polymer were shown in Table 1.

Comparative Example 2

The procedures were the same as those in Example 4, except that the catalyst was not subjected to pre-complexation. The main catalyst, co-catalyst (triethylaluminum) and external electron donor (methyl cyclohexyl dimethoxysilane) were fed separately to a prepolymerization reactor directly. The polymerization conditions and the performance of the polymer were shown in Table 1.

Comparative Example 3

The main catalyst (the solid active center component comprising titanium) was obtained by using the method described in Example 1 of Chinese patent CN200410062291.3 (including the content "Preparation of Particles of Magnesium Chloride/Alcohol Adduct" in Example 1 and "General Procedure for Preparing a Spheric Catalyst Component" before Example 1), wherein the internal electron donor compound was di-n-butyl phthalate. The obtained main catalyst contained 2.4 wt% of Ti, 18.0 wt% of magnesium, and 13 wt% of di-n-butyl phthalate.

Other operations were the same as those in Example 4. The polymerization conditions and the performance of the polymer were shown in Table 1.

0	1510	800	1510	1510	1510	1510
4	3.4	3.7	5.5	3.4	5.5	5.5
1	99.6	99.6	99.6	98.2	98.0	98.1
4	1.30	1.30	1.8	2.8	3.2	3.5
9	3.9	4.5	4.0	3.9	4.0	5.0
3	9.2	4	9.2	9.2	9.3	9.3
5	98	97	92	88	85	84
2	42	41	38	42	38	38

refers to the mass ratio of triethylaluminum to methyl cyclohexyl dimethoxysilane.

As could be seen from the above data, with respect to the selected catalyst of the present invention, the propylene-butene-1 random copolymer resulted by using the catalyst that had been subjected to pre-complexation treatment had a significant increase in the relative dispersity of butene-1 and a significant decrease in the xylene solubles content at room temperature, in comparison with the propylene-butene-1 random copolymer resulted by using the catalyst that had not been subjected to pre-complexation treatment. In the case of the same butene content, the copolymer had a similar transparency, but an increased heat distortion temperature. This demonstrated that the heat resistance of the material was improved. Moreover, as the pre-complexation time prolonged, the above effects could be further improved. As could be seen from the data of Comparative Example 3 and Example 4, the pre-complexation imposed a significant impact on the obtained performance of the selected catalyst of the present invention, that is to say, the selected catalyst of the present invention and the pre-complexation produced a synergistic effect.

Example 5 (a composition of the present invention)

The procedures of examples 1 to 4 and comparative examples 1 to 3 were repeated with the exception that 0.3 part by weight of nucleating agent Millad 3988 (Milliken Chemical Company, Ltd.), 0.1 parts by weight of IRGAFOS 168 additive (Ciba Specialty Chemicals), 0.2 parts by weight of IRGANOX 1010 additive (Ciba Specialty Chemicals) and 0.05 parts by weight of calcium stearate (Ciba Specialty Chemicals) were added respectively into each 100 parts by weight of the obtained polymer powders and then granulated by two-screw extruder, thereby obtaining the pellets of the compositions 1 to 4 (Comp. 1-4) and comparative compositions 1 to 3 (Comparative Comp. 1-3). The

performances of the compositions were shown in Table 2.

Table 2 Overview of performances of compositions

	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comparative Comp. 1	Comparative Comp. 2	Comparative Comp. 3
Heat distortion temperature, □	101	106	106	98	93	88	86
Haze, %	7.6	7.5	7.4	6.0	7.7	6.2	6.2
n-Hexane extract, g/100g	0.8	0.7	0.7	1.0	1.1	1.3	1.4

As could be seen from Table 2, the composition prepared from the propylene-butene-1 random copolymer having a higher relative dispersity of butene-1 and a lower xylene solubles content after the addition of a nucleating agent had better transparency and heat resistance and lower migrants content.

Example 6 (food packaging container of the present invention)

The food packaging container of the present invention was produced by an injection moulding process. In this process, the pellets of composition 1 as prepared in Example 5 were dried in a thermostatic oven at temperature of 90□ for 4 hours. The materials were turned into a molten state in cylinder of the injection machine by the homogeneous heating. Under a certain pressure and injection rate, a defined amount of molten materials were injected into the mold cavity, subjected to a pressure keeping stage and then cooled to be solidified to a shaped article. During the whole injection moulding process the following parameters and conditions were adopted: the temperature of injection machine being

190℃ ~ 220℃, the injection pressure being 50 ~ 60 MPa, dwell pressure being 50 ~ 60 MPa, dwell time being 30 ~ 40 seconds, cooling time being 15 ~ 20 seconds and the mold temperature being 35 ~ 45℃.

Claims

1. A propylene-butene-1 random copolymer, characterized in that it has a butene-1 content of 1-6 mol%, preferably 3-6 mol%, and has a relative dispersity of butene-1, as determined by Nuclear Magnetic Resonance (NMR), of greater than 98.5%, preferably greater than 99.0% wherein the relative dispersity is measured under the following conditions using a 400 MHz NMR machine:

deuterated o-dichlorobenzene as solvent,

250 mg sample / 2.5 ml solvent,

dissolving sample at 140℃,

collecting ^{13}C-NMR,

detection temperature 125℃,

detection head 10mm,

delay time D1 being 10 seconds,

sampling time AT being 5 seconds,

scanning times > 5000 times;

and further characterized in that the propylene-butene-1 random copolymer is obtained by copolymerization with the use of a Ziegler-Natta catalyst comprising a main catalyst component A, a co-catalyst component B and an external electron donor component C, wherein the component A is a solid catalyst component comprising titanium and a polybasic carboxylic acid ester obtained by dissolving magnesium halide in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent;

the component B is an alkyl aluminum compound having the general formula AlR_nX_{3-n}, wherein R is hydrogen or a hydrocarbon group having 1 to 20 carbon atoms, X is halogen; and

the component C is an organosilicon compound having the general

formula $R_nSi(OR')_{4-n}$, where $0 \leq n \leq 3$, R and R' are the same or different alkyl groups, cycloalkyl groups, aryl groups or halogenated alkyl groups;

wherein the three catalyst components A, B and C are subjected to pre-complexation and optional pre-polymerization and then added to the reactor

2. The propylene-butene-1 random copolymer as claimed in claim 1, characterized in that it has a xylene solubles content at room temperature measured according to ASTM D5492-98, which is lower than the following fitted line: Y = 0.77 +0.252X, wherein Y is the weight percent of the xylene solubles at room temperature, and X is the mole percent of butene-1 in the propylene-butene-1 random copolymer.

3. The propylene-butene-1 random copolymer as claimed in claim 1 or claim 2, characterized in that it has a melt index, according to ISO 1133 at 230℃ under a load of 2.16 kg, of 0.5-50 g/10 min, preferably 2-30 g/10 min.

4. The propylene-butene-1 random copolymer as claimed in any one of claims 1-3, characterized in that it has a molecular weight distribution index Mw/Mn, as measured according to GPC, of 3.5-8, preferably 3.8-6.

5. The propylene-butene-1 random copolymer as claimed in claim 1, characterized in that, in the solvent system, based on per mole of the magnesium halide, the amount of the organic epoxy compound is 0.2-5 moles, and the mole ratio of the organic epoxy compound to the organic phosphorus compound is 0.9-1.6.

6. The propylene-butene-1 random copolymer as claimed in claim 1 or

claim 6, characterized in that, the mole ratio of the component B to the component A, measured as the mole ratio of aluminum to titanium, is 5-1000, and the ratio of the component C to the component A, measured as the mole ratio of silicon to titanium, is 2-100.

7. The propylene-butene-1 random copolymer as claimed in any one of claims 1-6, characterized in that the main catalyst component A is obtained by dissolving magnesium halide in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent to form a homogeneous solution, mixing the solution with titanium halide or a derivative thereof to precipitate a solid in the presence of a precipitating agent, treating the solid with a polybasic carboxylic acid ester to make it loaded onto the solid, and then treating the solid with titanium tetrahalide and an inert diluent, wherein the precipitating agent is one selected from an organic acid anhydride, an organic acid, an ether and a ketone.

8. The propylene-butene-1 random copolymer as claimed in any of claims 1-7, characterized in that, in the homogeneous solution formed from magnesium halide useful for preparing the component A, based on per mole of magnesium halide, the amount of the organic epoxy compound is 0.6-2 moles; the mole ratio of the organic epoxy compound to the organic phosphorus compound is 0.9-1.4; the amount of the inert diluent is 1200-2400 ml.

9. The propylene-butene-1 random copolymer as claimed in any one of claims 1-8, characterized in that the magnesium halide useful for preparing the component A is one selected from magnesium dihalide, complexes of magnesium dihalide with water or alcohol, and derivatives obtained by replacing one halogen atom in the molecular formula of

magnesium dihalide with hydrocarbon group or halohydrocarbyloxy group, or a mixture thereof.

10. The propylene-butene-1 random copolymer as claimed in any one of claims 1-9, characterized in that the organic epoxy compound useful for preparing the component A is one selected from ethylene oxide, propylene oxide, butylene oxide, butadiene oxide, butadiene dioxide, epichlorohydrin, methyl glycidyl ether, diglycidyl ether, tetrahydrofuran, or a mixture thereof.

11. The propylene-butene-1 random copolymer as claimed in any one of claims 1-10, characterized in that the organic phosphorus compound useful for preparing the component A is one selected from trimethyl ortho-phosphate, triethyl ortho-phosphate, tributyl ortho-phosphate, triphenyl ortho-phosphate, trimethyl phosphite, triethyl phosphite, tributyl phosphite, benzyl phosphite, or a mixture thereof.

12. The propylene-butene-1 random copolymer as claimed in any one of claims 7-11, characterized in that the precipitating agent useful for preparing the component A is one selected from acetic anhydride, phthalic anhydride, succinic anhydride, maleic anhydride, pyromellitic dianhydride, acetic acid, propionic acid, butyric acid, acrylic acid, methacrylic acid, acetone, methyl ethyl ketone, benzophenone, methyl ether, ethyl ether, propyl ether, butyl ether, amyl ether, or a mixture thereof.

13. The propylene-butene-1 random copolymer as claimed in any one of claims 1-12, characterized in that the polybasic carboxylic acid ester useful for preparing the component A is one selected from diethyl malonate, dibutyl malonate, diethyl adipate, dibutyl adipate, diethyl

sebacate, dibutyl sebacate, diisobutyl phthalate, di-n-butyl phthalate, diisooctyl phthalate, diethyl maleate, di-n-butyl maleate, diethyl naphthalene dicarboxylate, dibutyl naphthalene dicarboxylate, triethyl trimellitate, tributyl trimellitate, triethyl hemimellitate, tributyl hemimellitate, tetraethyl pyromellitate, tetrabutyl pyromellitate.

14. The propylene-butene-1 random copolymer as claimed in any one of claims 7-13, characterized in that the titanium halide or its derivative useful for preprating the component A is one selected from titanium tetrachloride, titanium tetrabromide, titanium tetraiodide, tetrabutoxy titanium, tetraethoxy titanium, monochloro triethoxy titanium, dichloro diethoxy titanium, trichloro monoethoxy titanium, or a mixture thereof.

15. The propylene-butene-1 random copolymer as claimed in any one of claims 1-14, characterized in that the method for preparing the catalyst component A comprises the following steps:

1). Magnesium halide is dissolved with stirring in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent at a temperature of 0-100℃ to form a transparent homogeneous solution;

2). In the presence of a precipitating agent and at a temperature of -35-60℃, a titanium compound is added to the magnesium halide solution or the magnesium halide solution is added to a titanium compound, and moreover, a polybasic carboxylic acid ester needs to be added before or after the precipitation of a solid to thereby treat the precipitated solid and make the polybasic carboxylic acid ester partially loaded on the solid;

3). The reaction mixture is heated to a temperature of 60-110℃, and the suspension is stirred at this temperature for 10 minutes to 10 hours;

4). After end of the stirring, the solid is precipitated from the mixture solution, followed by filtering, removing mother liquor, and washing the solid with toluene and hexane, to obtain the solid catalyst component A comprising titanium.

16. The propylene-butene-1 random copolymer as claimed in claim 1, characterized in that the pre-complexation temperature is controlled in the range of -10-60℃, preferably in the range of 0-30℃.

17. The propylene-butene-1 random copolymer as claimed in claim 1 or claim 16, characterized in that the pre-complexation time is 0.1-100 min, preferably 1-30 min.

18. The propylene-butene-1 random copolymer as claimed in any one of claims 1-17, characterized in that the copolymerization of propylene and butene-1 is carried out in a liquid phase loop reactor.

19. A method for preparing a propylene-butene-1 random copolymer according to any one of claims 1-18, characterized in that propylene and butene-1 are copolymerized by adjusting the amount of the comonomer butene-1 added in the reactor, in the presence of a Ziegler-Natta catalyst comprising a main catalyst component A, a co-catalyst component B and an external electron donor component C, at a polymerization temperature and with an appropriate hydrogen content;

wherein the component A is a solid catalyst component comprising titanium and a polybasic carboxylic acid ester obtained by dissolving magnesium halide in a solvent system composed of an organic epoxy compound, an organic phosphorus compound and an inert diluent;

the component B is an alkyl aluminum compound having the general

formula AlR_nX_{3-n}, wherein R is hydrogen or a hydrocarbon group having 1 to 20 carbon atoms and X is halogen; and

the component C is an organosilicon compound having the general formula $R_nSi(OR')_{4-n}$, where $0 \leq n \leq 3$, R and R' are the same or different alkyl groups, cycloalkyl groups, aryl groups or halogenated alkyl groups;

and in that the three catalyst components A, B and C are subjected to pre-complexation and optional pre-polymerization and then added to the reactor.

20. A propylene-butene-1 random copolymer composition, which comprises the propylene-butene-1 random copolymer as claimed in any one of claims 1-18 and 0.1-1 parts by weight, preferably 0.2-0.4 parts by weight, of a nucleating agent, in relative to 100 parts by weight of the propylene-butene-1 random copolymer.

21. The propylene-butene-1 random copolymer composition as claimed in claim 20, characterized in that the nucleating agent is Millad 3988 nucleating agent, ADK NA-21 nucleating agent and Millad NX8000 nucleating agent.

22. The propylene-butene-1 random copolymer composition as claimed in claim 20 or claim 21, characterized in that a sheet with a thickness of 1 mm formed from the composition by melt injection molding has a haze of less than 10%, preferably less than 8%.

23. The propylene-butene-1 random copolymer composition as claimed in any one of claims 20-22, characterized in that the composition has heat distortion temperature of greater than 95℃, preferably greater than 100℃, more preferably greater than 105℃.

24. A method for preparing the propylene-butene-1 random copolymer composition as claimed in any one of claims 20-23, which comprises the step of melt blending the propylene-butene-1 random copolymer powder with a nucleating agent and optionally other additives.

25. A food packaging container, which is formed by the propylene-butene-1 random copolymer as claimed in any one of claims 1-18 or the propylene-butene-1 random copolymer composition as claimed in any one of claims 20-24.