

Description

This invention relates to high-strength polypropylene fiber.

The most widespread technique for enhancing the strength of polypropylene fiber comprises increasing the draft ratio. In addition, various studies on stretching conditions, spinning conditions, molecular weight of polypropylene and the like have been conducted for the same purpose.

For example, Japanese Patent Publication No. 54-32855 discloses a method comprising decreasing the molecular weight of polypropylene within a pelletizer.

EP-A-0151883 claims a crystalline propylene polymer composition comprising a blend of crystalline polypropylene with a polymer of a vinyl cycloalkane having at least 6 C-atoms; the composition contains 0.05 to 10,000 ppm by weight of the vinyl cycloalkane unit. The polypropylene may be a homopolymer or a random copolymer with another α -olefin having 2 to 18 C-atoms. The vinyl cycloalkane polymer may be a homopolymer or a copolymer with an α -olefin. Fibers made of such compositions are also disclosed.

However, each of the conventional techniques has a limit in achievement of strength of polypropylene fiber, and there is a need to further improve strength of polypropylene fiber.

One object of this invention is to provide polypropylene fiber having improved strength.

The inventors have found that polypropylene having incorporated therein a vinylcycloalkane polymer prepared in specific manner provides polypropylene fiber having high strength than the conventional polypropylene fiber.

According to the invention we provide high-strength polypropylene fiber obtainable from polypropylene having incorporated therein from 0.05 to 10,000 ppm by weight of a vinylcycloalkane polymer, wherein said polypropylene is polypropylene preparable by degrading a propylene homopolymer or a copolymer comprising propylene as comonomeric unit and up to 5 mol% of other α -olefins as comonomeric unit, the undegraded polymers having an intrinsic viscosity of from 1.1 to 3.5 dl/g as measured in a tetralin solution at 135°C, with an organic peroxide or by heating, characterised in that the polypropylene is degraded so as to have its intrinsic viscosity reduced to 1/5 to 7/10.

The vinylcycloalkane polymer which can be used in the present invention includes vinylcycloalkane homopolymers, copolymers comprising different kinds of vinylcycloalkanes, and copolymers comprising vinylcycloalkanes and up to 20 mol% of α -olefin or styrene comonomeric units.

The vinylcycloalkane polymers to be used are not limited as to how they are produced and may be obtained by radical polymerisation, cationic polymerization, anionic polymerization, coordination anionic polymerization, and the like. Of these techniques, the most preferred is coordination anionic polymerization, which is preferably carried out in the presence of a Ziegler-Natta catalyst composed of a transition metal compound and an organometallic compound that is commonly employed for polymerization of α -olefins.

The vinylcycloalkane polymers can also be obtained by hydrogenation of styrene polymers.

Specific examples of vinylcycloalkanes as monomer include vinylcyclopentane, vinylcyclohexane, vinylcyclooctane, 2-methylvinylcyclohexane, 3-methylvinylcyclohexane, 4-methylvinylcyclohexane, 3-ethylvinylcyclohexane, 4-ethylvinylcyclohexane, allylcyclopentane and allylcyclohexane.

The α -olefins and styrenes which can be copolymerized with the vinylcycloalkanes contain from 2 to 18 carbon atoms and specifically include α -olefins, e.g., ethylene, propylene, butene-1, octene-1, decene-1, 3-methylbutene-1, 4-methylpentene-1 or 5-methylhexene-1; and styrenes, e.g., styrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene or 4-ethylstyrene.

The polypropylene having incorporated therein the above-described vinylcycloalkane polymer can be prepared as follows.

(1) Method comprising blending the vinylcycloalkane polymer and polypropylene:

For blending, usual polymer blending techniques are employed to advantage. That is, powders or pellets of both polymers are mixed, and the mixture is kneaded while the polypropylene is molten; or the vinylcycloalkane polymer and polypropylene both in a dissolved state are mixed, and then the solvent is removed.

(2) A method comprising homo- or copolymerizing a vinylcycloalkane by using a catalyst for coordination anionic polymerization in a first stage and then homopolymerizing propylene or copolymerizing propylene and other α -olefins in a second stage.

(3) The method of (2) above, in which the order of polymerization is reversed, or each of the first and second stages is repeated.

(4) A method comprising blending the vinylcycloalkane polymer-containing polypropylene as obtained in the method (2) or (3) above with ordinary polypropylene.

The polypropylene which can be used in the present invention is crystalline and includes a propylene homopolymer and a copolymer comprising propylene and up to 5 mol% of other α -olefins. The α -olefins

herein used preferably include those recited as comonomers of the vinylcycloalkane copolymers. Furthermore, there may be used a polypropylene to which a vinyl-containing compound, e.g., maleic anhydride, or styrene is grafted. For suitability for spinning and drafting, the undegraded polypropylene has an intrinsic viscosity $[\eta]$ of from 1.1 to 3.5 dl/g as measured in a tetralin solution at 135°C. The intrinsic viscosity of the polypropylene is further reduced to 1/5 to 7/10 by heating or with an organic peroxide, etc.

The vinylcycloalkane polymer-containing polypropylene according to the present invention can be spun and stretched under the same conditions as used for ordinary propylene polymers. For example, it is spun at a temperature of from 200 to 280°C and stretched at a temperature of from 50 to 150°C, and it may further contain various additives generally employed, such as fillers and dye-assist agents.

The present invention is now illustrated in greater detail with reference to the following examples, but it should be understood that the present invention is not deemed to be limited thereto. In these examples, all percentages and parts are by weight unless otherwise indicated.

EXAMPLES 1 TO 3

1) Synthesis of Vinylcyclohexane Polymer-Containing Polypropylene:

To 1,000 ml of dehydrated n-heptane were successively added 2.0 g of diethylaluminum chloride and 25.0 g of a titanium trichloride catalyst (product of Marubeni-Solvay Co., Ltd.) in a nitrogen gas atmosphere. The mixed solution was heated to 60°C, and 350 ml of vinylcyclohexane was added dropwise thereto while stirring to effect polymerization for 2.5 hours. The thus formed slurry was washed with n-heptane and dried under reduced pressure to obtain a polymer powder (9.85 g of vinylcyclohexane was polymerized per gram of the titanium trichloride catalyst).

In the presence of 252 g of the resulting powder containing the activated titanium trichloride catalyst and 180 g of diethylaluminum chloride, propylene was homopolymerized in 150 l of n-heptane at 60°C for 1.5 hours at a gauge pressure of 8.8×10^5 Pa (9 kg/cm²) and at a hydrogen partial pressure of 0.6×10^5 Pa (0.6 kg/cm²).

After completion of the polymerization, the catalyst was deactivated and deashed by using n-butanol to recover polypropylene (1045 g of propylene was polymerized per gram of the titanium trichloride catalyst).

The vinylcyclohexane polymer content in the resulting polymer was calculated from the amounts of the polymerized vinylcyclohexane and polymerized propylene and found to be 0.94wt%. The resulting polymer had a $[\eta]$ of 1.7 dl/g.

2) Spinning Polypropylene Pellets:

To 100 parts of an ordinary propylene homopolymer having a $[\eta]$ of 2.7 dl/g was added 0.065 part (Example 1), 0.65 part (Example 2), or 6.5 parts (Example 3) of the polymer powder as prepared in (1) above. To each of the mixture were further added 0.1 part of tetrakis-[methylene-3(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate] methane ("Irganox®1010" produced by Ciba-Geigy AG), 0.2 part of distearyl-3,3'-thiodipropionate ("Sumilizer® TPS" produced by Sumitomo Chemical Co., Ltd.), 0.5 part of 2-(2-hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole ("Sumisorb® 300" produced by Sumitomo Chemical Co., Ltd.), and as a molecular weight reducing agent 0.1 part of 2,5-dimethyl-2,5-di-(t-butylperoxy)-hexane, and the mixture was kneaded and pelletized. The resulting pellets had a $[\eta]$ of 0.91 dl/g, 0.89 dl/g, or 0.91 dl/g, respectively.

3) Spinning and Stretching

The pellets obtained in (2) above were spun at 240°C by the use of a spinning machine of screw gear pump type at a take-up speed of 280 m/min. The undrafted spun filaments were stretched at 110°C at a stretch ratio of 3. The resulting stretched filament was determined for fiber strength, and the results obtained are shown in Table 1.

COMPARATIVE EXAMPLE 1

Drafted filaments were obtained in the same manner as in Example 1, except that the vinylcyclohexane polymer-containing polymer powder as prepared in Example 1-(1) was not used. The fiber strength of the resulting filaments is shown in Table 1.

TABLE 1

Example No.	Vinylcyclohexane Polymer Content (ppm)	Drafted Filaments		
		Fineness (d)	Fiber Strength (g/d)	Elongation (%)
Example 1	6	16	2.2	88
Example 2	60	16	2.4	106
Example 3	573	15	2.5	93
Comparative Example 1	-	18	1.8	91

As described above, there is provided by the present invention polypropylene fibers having improved strength.

Claims

1. High-strength polypropylene fiber obtainable from polypropylene having incorporated therein from 0.05 to 10,000 ppm by weight of a vinylcycloalkane polymer, wherein said polypropylene is polypropylene preparable by degrading a propylene homopolymer or a copolymer comprising propylene as comonomeric unit and up to 5 mol% of other α -olefins as comonomeric unit, the undegraded polymers having an intrinsic viscosity of from 1.1 to 3.5 dl/g as measured in a tetralin solution at 135°C, with an organic peroxide or by heating, characterised in that the polypropylene is degraded so as to have its intrinsic viscosity reduced to 1/5 to 7/10.
2. High-strength polypropylene fiber as claimed in Claim 1, wherein said polypropylene is a propylene homopolymer or a copolymer comprising propylene and up to 5 mol% of other α -olefins.
3. High-strength polypropylene fiber as claimed in Claim 1 or 2, wherein said vinylcycloalkane polymer is a vinylcycloalkane homopolymer, a copolymer comprising different kinds of vinylcycloalkanes, or a copolymer comprising a vinylcycloalkane and up to 20 mol% of α -olefin or styrene monomers as comonomeric unit.

Patentansprüche

1. Polypropylenfasern mit hoher Festigkeit, erhältlich aus Polypropylen mit einem Zusatz von 0,05 bis 10 000 Gew.-Teilen pro Millionen (ppm) eines Vinylcycloalkanpolymers, wobei das Polypropylen herstellbar ist durch Abbau eines Propylenhomopolymers oder eines Copolymers, umfassend Propylen als comonomere Einheit und bis zu 5 Mol-% andere α -Olefine als comonomere Einheit, mit einem organischen Peroxid oder durch Erhitzen, und die nicht abgebauten Polymere eine intrinsische Viskosität von 1,1 bis 3,5 dl/g, gemessen in einer Tetralinlösung bei 135°C aufweisen, dadurch gekennzeichnet, daß das Polypropylen soweit abgebaut wird, daß seine intrinsische Viskosität auf 1/5 bis 7/10 vermindert ist.
2. Polypropylenfasern mit hoher Festigkeit nach Anspruch 1, wobei das Polypropylen ein Propylenhomopolymer oder ein Copolymer, umfassend Propylen und bis zu 5 Mol-% andere α -Olefine, ist.
3. Polypropylenfasern mit hoher Festigkeit nach Anspruch 1 oder 2, wobei das Vinylcycloalkanpolymer ein Vinylcycloalkanhomopolymer, ein Copolymer, umfassend verschiedene Arten von Vinylcycloalkanen oder ein Copolymer, umfassend ein Vinylcycloalkan und bis zu 20 Mol-% α -Olefin- oder Styrolmonomere als comonomere Einheit, ist.

Revendications

1. Fibre de polypropylène de résistance élevée que l'on peut obtenir à partir de polypropylène dans lequel est incorporé de 0,05 à 10 000 ppm en poids d'un polymère de vinylcycloalcane, dans lequel ledit polypropylène est un polypropylène que l'on peut préparer en dégradant un homopolymère de polypropylène ou un copolymère comprenant du propylène en tant qu'unité comonomérique et jusqu'à



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3. High-strength polypropylene fiber as claimed in Claim 1 or 2, wherein said vinylcycloalkane polymer is a vinylcycloalkane homopolymer, a copolymer comprising different kinds of vinylcycloalkanes, or a copolymer comprising a vinylcycloalkane and up to 20 mol% of α -olefin or styrene monomers as comonomeric unit.

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1. Polypropylenfasern mit hoher Festigkeit, erhältlich aus Polypropylen mit einem Zusatz von 0,05 bis 10 000 Gew.-Teilen pro Millionen (ppm) eines Vinylcycloalkanpolymers, wobei das Polypropylen herstellbar ist durch Abbau eines Propylenhomopolymers oder eines Copolymers, umfassend Propylen als comonomere Einheit und bis zu 5 Mol-% andere α -Olefine als comonomere Einheit, mit einem organischen Peroxid oder durch Erhitzen, und die nicht abgebauten Polymere eine intrinsische Viskosität von 1,1 bis 3,5 dl/g, gemessen in einer Tetralinlösung bei 135°C aufweisen, dadurch gekennzeichnet, daß das Polypropylen soweit abgebaut wird, daß seine intrinsische Viskosität auf 1/5 bis 7/10 vermindert ist.
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3. Polypropylenfasern mit hoher Festigkeit nach Anspruch 1 oder 2, wobei das Vinylcycloalkanpolymer ein Vinylcycloalkanhomopolymer, ein Copolymer, umfassend verschiedene Arten von Vinylcycloalkanen oder ein Copolymer, umfassend ein Vinylcycloalkan und bis zu 20 Mol-% α -Olefin- oder Styrolmonomere als comonomere Einheit, ist.

Revendications

1. Fibre de polypropylène de résistance élevée que l'on peut obtenir à partir de polypropylène dans lequel est incorporé de 0,05 à 10 000 ppm en poids d'un polymère de vinylcycloalcane, dans lequel ledit polypropylène est un polypropylène que l'on peut préparer en dégradant un homopolymère de polypropylène ou un copolymère comprenant du propylène en tant qu'unité comonomérique et jusqu'à



5% en mole d'autres α -oléfines en tant qu'unités comonomériques, les polymères non dégradés ayant une viscosité intrinsèque comprise entre 1,1 et 3,5 dl/g mesurée dans une solution de tétraline à 135°C, à l'aide d'un peroxyde organique ou par chauffage, caractérisée en ce que le polypropylène est dégradé de sorte que sa viscosité intrinsèque est ramenée jusqu'à 1/5 à 7/10.

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2. Fibre de polypropylène de résistance élevée selon la revendication 1, dans laquelle ledit polypropylène est un homopolymère de propylène ou un copolymère comprenant du propylène et jusqu'à 5% en mole d'autres α -oléfines.

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3. Fibre de polypropylène de résistance élevée selon la revendication 1 ou 2, dans lequel ledit polymère de vinylcycloalcane est un homopolymère de vinylcycloalcane, un copolymère comprenant différents types de vinylcycloalcane ou un copolymère comprenant un vinylcycloalcane et jusqu'à 20% de monomères constitués d' α -oléfine ou de styrène en tant qu'unités comonomériques.

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