

WHOLLY AROMATIC POLYAMIDE FIBERS AND
PRODUCTION PROCESS OF SAME

BACKGROUND OF THE INVENTION.

5 1. Field of the Invention

 The present invention relates to wholly aromatic polyamide fibers containing a layer-structured clay mineral, and a production process thereof. More particularly, the present invention relates to wholly aromatic polyamide fibers containing a layer-structured clay mineral and having improved mechanical characteristics, particularly toughness, and a production process thereof.

15 2. Description of the Related Art

 Considerable interest has been focused on the imparting of high added value to polymers and enhancement of their performance in recent years. Compound materials obtained by containing a filler in a polymer have been actively developed in order to impart high added value and high performance to polymers. In the past, fibrous or acicular fillers have been used as reinforcing fillers for the purpose of improving the mechanical characteristics and heat resistance of polymers and, as a result, known polymer materials are improved in terms of tensile strength, modulus of elasticity, bending strength, thermal dimensional stability and creep characteristics as well as in terms of various other properties such as improved warping, wear resistance, surface hardness, heat resistance and impact resistance.

30 However, the strength of a compound material is known to be greatly affected not only by the strength of the polymer serving as the matrix of the compound material as well as the strength of the filler itself, but also by the interface adhesion between the filler and polymer, and the quality of the wettability of the polymer to the filler has an effect not only on the ease of production, but also on the strength of the finished

product. For reasons such as these, it is not always possible to obtain a compound material having superior strength even if a filler or polymer having high strength and elasticity is used for the material.

5 Moreover, compound materials containing a filler are generally known to have the disadvantage of low ultimate elongation.

10 On the other hand, in the production process of wholly aromatic polyamide fibers (to be referred to as aramid fibers), there is a desire to further improve process stability and quality (prevention of filament breakage). In general, a toughness factor (TF) is typically known to be used as a parameter for evaluating industrial aramid fibers. Toughness factor (TF) is
15 represented by the product of tensile strength (T') as measured in units of grams/denier and the square root of ultimate elongation (%) ($TF = T' \times E^{1/2}$). In the case of fibers having a high toughness factor, the amount of the fibers retained on the drawing roll in the drawing
20 process is known to decrease, and as a result, filament breakage in the resulting fibers is reduced resulting in improvement of stability of the drawing process and improved quality of the resulting fiber threads.

25 Although a known example of a process for improving fiber mechanical strength involves improving the degree of orientation of fibers by drawing, in the case of using such a process, as ultimate elongation is known to decrease with the improvement tensile strength, it becomes difficult to produce filaments having a high
30 toughness factor.

 In the past, containing a filler in the form of a layer-structured clay mineral was proposed to improve the mechanical properties and dimensional stability of polyamide fibers (see Japanese Unexamined Patent
35 Publication Nos. H3-31364, H4-209882 and H8-3818). However, these are all targeted at thermoplastic polyamide, and the use of a layer-structured clay mineral

for non-thermoplastic polyamide, in the form of wholly aromatic polyamide fibers, is not disclosed in these patent documents.

5 In addition, processes using layer-structured clay minerals as fillers have been examined for the purpose of improving the mechanical characteristics and heat resistance of wholly aromatic polyamide. For example, Japanese Unexamined Patent Publication No. H11-236501 discloses a process for obtaining a wholly aromatic
10 polyamide compound material that is useful as a highly heat-resistant material by mixing an aqueous solution containing a diamine monomer and an organic solvent solution of an acylated dicarboxylic acid monomer that is soluble in water, and adding a clay mineral to the
15 aqueous solution or organic solvent solution during polycondensation of the monomers, Japanese Unexamined Patent Publication No. H11-255839 discloses a process for efficiently obtaining a compound by solution polymerizing a wholly aromatic polyamide in a solvent solution of a
20 layer-structured clay mineral capable of completely dissolving said layer-structured clay mineral, while Japanese Unexamined Patent Publication No. H11-256034 proposes a process for obtaining a wholly aromatic polyamide compound having improved mechanical properties
25 in which a layer-structured clay mineral is highly and finely dispersed in a wholly aromatic polyamide by removing an organic solvent from a solution composed of the wholly aromatic polyamide, the layer-structured clay mineral and the organic solvent.

30 However, the improvement of the mechanical properties of wholly aromatic polyamide fibers by containing a layer-structured clay mineral as filler, and wholly aromatic polyamide fibers containing a layer-structured clay mineral as filler and having a high
35 toughness factor as a result of thereof, are not known from documents of the prior art.

SUMMARY OF THE INVENTION

An object of the present invention is to provide wholly aromatic polyamide fibers having high mechanical properties, and a high toughness factor in particular, that can be spun with satisfactory process stability in a spinning process, and a process for industrially producing the same.

According to research conducted by the inventors of the present invention, drawn and oriented wholly aromatic polyamide fibers obtained by wet spinning and drawing a spinning liquid containing a wholly aromatic polyamide and a layer-structured clay mineral were found to have superior mechanical characteristics, and particularly superior toughness factor. More surprisingly, it was also found by the inventors of the present invention that, instead of completely uniformly dispersing each layer of the layer-structured clay mineral in the fibers, by scatteringly distributing a plurality of regions having a relatively high layer-structured clay mineral distribution density in the aromatic polyamide polymer matrix that composes the particles, the effect of improving the mechanical characteristics of the fibers, and particularly the toughness factor, can be further enhanced by the layer-structured clay mineral particles.

Drawn and oriented wholly aromatic polyamide fibers of the present invention comprise a resin composition comprising a matrix composed of a wholly aromatic polyamide resin and layer-structured clay mineral particles dispersed and distributed in an amount of 0.05 to 20 parts by mass, based on 100 parts by mass of the matrix, in the matrix.

In the wholly aromatic polyamide fibers of the present invention, a plurality of regions, in which the layer-structured clay mineral particles are distributed in a relatively high distribution density, are preferably scatteringly distributed in the wholly aromatic polyamide matrix.

In the wholly aromatic polyamide fibers of the

present invention, when the wholly aromatic polyamide fibers are cross-cut along the fiber axes, the resultant cross-sectional profiles are observed with an electronic microscope at a magnification of 100,000, and in each cross-sectional profile, a total area S1 of a plurality of regions in which regions a change in conditions of the fiber cross-sectional profile due to an influence of the layer-structured clay mineral particles distributed in the observation area S2 of $25 \mu\text{m}^2$ is found, is measured, the degree of dispersion Y of the layer-structured clay mineral particles in each fiber, defined by the equation (1):

$$Y(\%) = (S1/S2) \times 100 \quad (1)$$

is preferably in the range of from 0.1 to 40.

In the wholly aromatic polyamide fibers of the present invention, the layer-structured clay mineral preferably comprises at least one selected from hectorite, saponite, stevensite, beidellite, montmorillonite and swelling mica.

In the wholly aromatic polyamide fibers of the present invention, the layer-structured clay mineral particles are preferably ones treated with an intercalating agent.

In the wholly aromatic polyamide fibers of the present invention, the layer-structured clay mineral particles preferably have an average layer thickness of 10 to 500 nm.

In the wholly aromatic polyamide fibers of the present invention, the layer-structured clay mineral particles preferably have a degree of orientation A of 50% or more, determined in accordance with the equation (2):

$$A(\%) = [(180 - w)/180] \times 100 \quad (2)$$

in equation (2), w represents a half value width of an intensity distribution determined, in an X-ray analysis of the layer-structured clay mineral particles, along a

Debye ring of a reflection peak in a (001) plane of the layer-structured clay mineral particles.

In the wholly aromatic polyamide fibers of the present invention, a ratio (T/To) of a tensile strength (T) of the wholly aromatic polyamide fibers to a tensile strength (To) of comparative wholly aromatic polyamide fibers identical to the wholly aromatic polyamide fibers except that the layer-structured clay mineral particles are not contained therein, is preferably 1.1 or more.

In the wholly aromatic polyamide fibers of the present invention, a ratio (E/Eo) of an ultimate elongation (E) of the wholly aromatic polyamide fibers to an ultimate elongation (Eo) of comparative wholly aromatic polyamide fibers identical to the wholly aromatic polyamide fibers except that the layer-structured clay mineral particles are not contained therein, is preferably 1.1 or more.

In the wholly aromatic polyamide fibers of the present invention, the toughness factor (TF) of the wholly aromatic polyamide fibers defined by the equation (3):

$$TF = T' \times E'^{1/2} \quad (3)$$

In which equation (3), T' represents a numeral value of the tensile strength in unit of g/1.1 dtex of the wholly aromatic polyamide fibers and E' represents a numeral value of the ultimate elongation in unit of % of the wholly aromatic polyamide fibers, is preferably 30 or more.

In the wholly aromatic polyamide fibers of the present invention, the ratio (TF/TFo) of the toughness factor (TF) of the wholly aromatic polyamide fibers to the tenacity factor (TFo) of comparative wholly aromatic polyamide fibers identical to the wholly aromatic polyamide fibers except that the layer-structured clay mineral particles are not contained therein, is preferably 1.1 or more.

In the wholly aromatic polyamide fibers of the

present invention, the layer-structured clay mineral particles preferably contain organic onium ions located between layers thereof.

5 In the wholly aromatic polyamide fibers of the present invention, the wholly aromatic polyamide resin is preferably selected from meta-wholly aromatic polyamide resins.

10 A process of the present invention for producing drawn and oriented wholly aromatic polyamide fibers comprises extracting a spinning liquid comprising a solvent and a wholly aromatic polyamide resin and layer-structured clay mineral particles in an amount of 0.05 to 20 parts by mass per 100 parts by mass of the wholly aromatic polyamide resin through a spinneret to form
15 filamentary streams of the spinning liquid;

Introducing the filamentary streams of the spinning liquid into an aqueous coagulation bath to coagulate the filamentary streams of the spinning liquid;

20 drawing the resultant undrawn filaments in a wetted atmosphere; and

dry-heat treating the resultant drawn filaments.

In the process of the present invention for producing wholly aromatic polyamide fibers, preferably the spinning liquid is prepared by mixing a solution A
25 comprising a portion of the solvent, a portion of the wholly aromatic polyamide resin and layer-structured clay mineral particles in an amount of 30 to 300 parts by mass per 100 parts by mass of the wholly aromatic polyamide resin with a solution B comprising the remaining portion
30 of the solvent, the remaining portion of the wholly aromatic polyamide resin, and satisfies the requirements (1) and (2):

(1) the viscosity of the solution (A) at a shear rate of 0.1 second^{-1} is 15 to 80 times the viscosity
35 thereof at a shear rate of 10 second^{-1} , and

(2) the viscosity of the solution (A) at a shear rate of 0.1 second^{-1} is 4 to 20 times the viscosity of the

solution (B) at a shear rate of 0.1 second^{-1} .

In the process of the present invention for producing wholly aromatic polyamide fibers, the concentration of the wholly aromatic polyamide resin in the spinning solution is preferably 0.1 to 30% by mass.

In the process of the present invention for producing wholly aromatic polyamide fibers, the draw ratio of the undrawn filaments in the wetted atmosphere is preferably in the range of 0.3 to 0.6 times the maximum draw ratio of the undrawn filaments.

In the process of the present invention for producing wholly aromatic polyamide fibers, the solvent is preferably selected from polar amide solvents.

In the process of the present invention for producing wholly aromatic polyamide fibers, the wholly aromatic polyamide resin is preferably selected from meta wholly aromatic polyamide resins.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an electron micrograph of a cross-section of one example of wholly aromatic polyamide fibers of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

In the wholly aromatic polyamide used in the present invention, the aromatic rings, from which the primary backbone of repeating units of the wholly aromatic polyamide is constituted, are mutually bonded through amide bonds, and the wholly aromatic polyamide is preferably selected from meta-wholly aromatic polyamides. This type of wholly aromatic polyamide is normally produced by low-temperature solution polymerization or interfacial polymerization of an aromatic dicarboxylic acid dihalide and an aromatic diamine in a solution thereof.

Although the diamine component used in the present invention preferably contains one or more types of, for example, paraphenylene diamine, 2-chloroparaphenylene diamine, 2,5-dichloroparaphenylene diamine, 2,6-

dichloroparaphenylene diamine, m-phenylene diamine, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl methane, 4,4'-diaminodiphenyl sulfone or 3,3'-diaminodiphenyl sulfone, it is not limited thereto.

5 Among these diamine compounds, p-phenylene diamine, m-phenylene diamine and 3,4'-diaminodiphenyl ether are used preferably.

In addition, although the aromatic dicarboxylic acid dihalide component used in the present invention
10 preferably contains one or more types of, for example, diisophthalic acid dichloride, terephthalic acid dichloride, 2-chloro-terephthalic acid dichloride, 2,5-dichloroterephthalic acid dichloride, 2,6-dichloroterephthalic acid dichloride or 2,6-naphthalene
15 dicarboxylic acid dichloride, it is not limited thereto. Among these aromatic dicarboxylic acid dihalides, terephthalic acid dichloride and/or isophthalic acid dichloride are used preferably.

Among the aforementioned wholly aromatic polyamides,
20 polymetaphenylene isophthalamide and copolyparaphenylene-3,4'-dioxydiphenylene terephthalamide are used preferably, while polymetaphenylene isophthalamide is used particularly preferably.

At least one type of solvent when preparing a
25 spinning liquid by polymerizing a wholly aromatic polyamide, examples of which include, but are not limited to, organic polar amide-based solvents such as N,N-dimethylformamide, N,N-dimethylacetoamide, N-methyl-2-pyrrolidone and N-methylcaprolactam, water-soluble ether
30 compounds such as tetrahydrofuran and dioxane, water-soluble alcohol compounds such as methanol, ethanol and ethylene glycol, water-soluble ketone compounds such as acetone and methyl ethyl ketone, and water-soluble nitrile compounds such as acetonitrile and propionitrile.
35 The aforementioned solvent may also be a mixture of two or more types of the aforementioned compounds. The solvent used in the process of the present invention is

preferably dehydrated.

In this case, a suitable amount of a conventionally known inorganic salt may be added to the polymerization mixture before polymerization, during polymerization or
5 at completion of polymerization in order to increase solubility. Examples of such inorganic salts include lithium chloride and calcium chloride.

In addition, when producing a wholly aromatic polyamide from the aforementioned diamine component and
10 the aforementioned acid halide component, the molar ratio of the diamine component to the acid halide component is preferably controlled to 0.90 to 1.10, and more preferably to 0.95 to 1.05.

A molecular terminal of a wholly aromatic polyamide used in the present invention may be blocked. In the case of using a terminal blocking agent for this purpose, examples of the blocking agent used include phthalic acid chloride and substituted forms thereof, while examples of the amine component include aniline and substituted forms
15 thereof.
20

In general, an aliphatic amine, aromatic amine and quaternary ammonium salt can be used in combination to capture an acid such as a hydrogen halide formed in reactions between acid halides and diamines.

25 Following completion of the aforementioned polymerization reaction, a basic inorganic compound such as sodium hydroxide, potassium hydroxide, calcium hydroxide or calcium oxide may be added to the reaction mixture as necessary to neutralize the reaction.

30 There are no special limitations on the reaction conditions for producing a wholly aromatic polyamide of the present invention. The reaction between the acid halide and diamine typically proceeds rapidly, and the reaction temperature is normally -25 to 100°C, and
35 preferably -10 to 80°C.

A wholly aromatic polyamide polymer obtained in this manner can be extracted in the form of pulp-like flakes

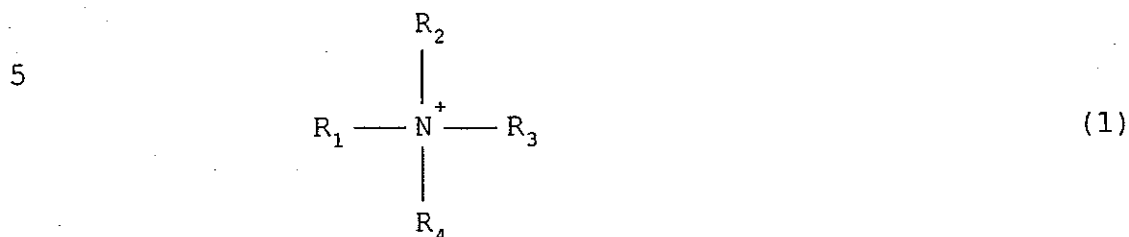
by charging and submerging it in a non-solvent such as water or alcohol. Although the polymer flakes can be redissolved in solvent and the resulting solution can be used for wet spinning, a solution obtained by a
5 polymerization reaction can also be used as is as a spinning liquid. Although there are no particular limitations on the solvent used when redissolving the polymer flakes provided it dissolves said wholly aromatic polyamide, a solvent used in polymerization of the
10 aforementioned wholly aromatic polyamide is used preferably.

Next, the layer-structured clay mineral used in the present invention has cation exchange ability and demonstrates the property of swelling as a result of
15 incorporating water between layers thereof, and a smectite clay mineral and swelling mica are used preferably. Specific examples of layer-structured clay minerals include smectite clay minerals such as hectorite, saponite, stevensite, beidelite and
20 montmorillonite (including their natural and chemically synthesized forms), as well as substituted forms, derivatives or mixtures thereof. In addition, examples of swelling mica include synthetic swelling mica that is chemically synthesized and has Li and Na ions between the
25 layers thereof, as well as substituted forms, derivatives or mixtures thereof.

In the present invention, layer-structured clay mineral particles that have been treated with a surface treatment agent containing organic onium ions
30 (intercalating agent) are preferably used for the aforementioned layer-structured clay mineral particles. Treatment with said organic onium ions improves the dispersivity of the wholly aromatic polyamide of the resulting layer-structured clay mineral particles in the
35 matrix, and is able to improve filament formability and the toughness factor of the resulting fibers.

The organic onium ion used in the aforementioned

surface treatment is preferably selected from quaternary ammonium ions having a chemical structure represented by the following formula (1):



10 (wherein, R_1 , R_2 , R_3 and R_4 respectively and independently represent an alkyl group having 1 to 30 carbon atoms or a hydroxypolyoxyethylene group represented by $-(CH_2CH_2O)_nH$. Here, alkyl groups having 1 to 18 carbon atoms are preferable among the alkyl groups having 1 to 30 carbon atoms represented by R_1 , R_2 , R_3 and R_4 .

15 Preferable examples of quaternary ammonium compounds used include, but are not limited to, dodecyl trimethyl ammonium chloride, tetradecyl trimethyl ammonium chloride, hexadecyl trimethyl ammonium chloride, octadecyl trimethyl ammonium chloride, oleyl trimethyl
20 ammonium chloride, didodecyl dimethyl ammonium chloride, ditetradecyl dimethyl ammonium chloride, dihexadecyl dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dioleyl dimethyl ammonium chloride, dodecyl diethylbenzyl ammonium chloride, tetradecyl
25 dimethylbenzyl ammonium chloride, hexadecyl dimethylbenzyl ammonium chloride, octadecyl dimethylbenzyl ammonium chloride, oleyl dimethylbenzyl ammonium chloride, trioctyl methyl ammonium chloride, hydroxypolyoxypropylene methyl diethyl ammonium chloride,
30 hydroxypolyoxyethylene dodecyl dimethyl ammonium chloride, hydroxypolyoxyethylene tetradecyl dimethyl ammonium chloride, hydroxypolyoxyethylene hexadecyl dimethyl ammonium chloride, hydroxypolyoxyethylene octadecyl dimethyl ammonium chloride,
35 hydroxypolyoxyethylene oleyl dimethyl ammonium chloride, dihydroxypolyoxyethylene dodecyl methyl ammonium chloride, bis(hydroxypolyoxyethylene) tetradecyl methyl

ammonium chloride, bis(hydroxypolyoxyethylene) hexadecyl methyl ammonium chloride, bis(hydroxypolyoxyethylene) octadecyl methyl ammonium chloride and bis(hydroxypolyoxyethylene) oleyl methyl ammonium chloride.

5 An example of a method for treating layer-structured clay mineral particles with organic onium ion normally consists of mixing 1 part by weight of layer-structured clay mineral particles and 1 to 10 parts by weight of organic onium ion in water followed by drying this
10 mixture. The amount of water used is preferably 1 to 100 times the amount of layer-structured clay mineral. In addition, the temperature during mixing is preferably 30 to 70°C, and the mixing time is preferably 0.5 to 2 hours. Preferable drying conditions consist of drying at normal
15 pressure for 3 days at 70 to 100°C and then vacuum drying for 2 days.

 The average layer thickness of the layer-structured clay mineral particles in the wholly aromatic polyamide fibers of the present invention is preferably 500 nm or
20 less and more preferably 200 nm or less. Furthermore, the average layer thickness of the layer-structured clay mineral referred to here indicates the average value of layer thickness as measured for all layer-structured clay mineral particles observed in a cross-sectional area of
25 25 μm^2 during measurement with an electron microscope (magnification: 100,000x) of longitudinal cross-sections of the fibers. If the average layer thickness of the layer-structured clay mineral is greater than 500 nm, it may be difficult to ensure forming stability during
30 spinning of the resulting resin composition. On the other hand, if it is attempted to disperse the layer-structured clay mineral particles are down to the molecular level, it is necessary to lower the concentration of the spinning liquid in order to ensure
35 thickening effects and dispersivity of the layer-structured clay mineral particles which, in addition to

lowering the production efficiency of the spinning process, also tends to reduce the effect of improving the toughness of the resulting fibers. Consequently, the average layer thickness of the layer-structured clay mineral particles is preferably 10 nm or more and more preferably 12 nm or more. In addition, the vertical and horizontal dimensions of the layer-structured clay mineral particles used in the present invention are preferably (50 to 1000 nm) × (50 to 1000 nm), and more preferably (100 to 500 nm) × (100 to 500 nm).

Moreover, when the total surface area S1 is measured at a plurality of regions, in which changes in the state of the fiber cross-sections are observed due to the effects of the layer-structured clay mineral particles, per an observed cross-sectional area S2 of 25 μm^2 , by cutting the wholly aromatic polyamide fibers along the fiber axes thereof and observing the longitudinal cross-sections with an electron microscope at a magnification of 100,000x, the degree of dispersion Y within each fiber of the layer-structured clay mineral particles as defined by the following formula (1):

$$Y(\%) = (S1/S2) \times 100 \quad (1)$$

is preferably within the range of 0.1 to 40 and more preferably within the range of 0.5 to 30. If the degree of dispersion Y is less than 0.1, there is little improvement in the toughness factor, while if the degree of dispersion Y exceeds 40, the transparency of the spinning liquid prepared from the wholly aromatic polyamide, layer-structured clay mineral particles and solvent becomes low and moldability decreases.

In the aforementioned microscopic observations, changes in the state of the fibers observed in the fiber cross-sections are caused by layer-structured clay mineral particles distributed in said cross-sectional regions being distributed at a higher distribution density as compared with other regions. It was first

found in the present invention that the toughness factor of the resulting fibers can be increased by scatteringly distributing regions having a relatively high distribution density of layer-structured clay mineral particles in the wholly aromatic polyamide polymer matrix of the fibers in this manner. The suitably scattered distribution of regions having a relatively high distribution density of layer-structured clay mineral particles can be achieved by controlling the degree of dispersion Y of the layer-structured clay mineral particles to within the range of 0.1 to 40.

Fig. 1 shows a cross-section of an example of a wholly aromatic polyamide drawn fiber of the present invention. In Fig. 1, a plurality of regions having a high distribution density of layer-structured clay mineral are observed to be scatteringly distributed in the form of staple fibers in the fiber cross-section. The staple fiber-like regions are elongated along the direction of the fiber axis.

Although the reason for the improvement in toughness factor of the resulting fibers as a result of scatteringly distributing regions having a relatively high distribution density of layer-structured clay mineral particles in the fibers as previously described is still not sufficiently clear, when these regions containing layer-structured clay mineral particles at a high distribution density are drawn, it is presumed that a network structure is formed by the layer-structured clay mineral particles and the wholly aromatic polyamide polymer molecules, and this network structure is oriented along the direction of the fiber axes due to drawing. The formation of this network structure oriented between the layer-structured clay mineral particles and polymer is thought to greatly contribute to improvement of toughness factor even if the content of the layer-structured clay mineral particles is relatively small.

In the present invention, fillers other than the

layer-structured clay mineral can be used in combination in the wholly aromatic polyamide polymer provided they are within a range that does not impair physical properties or process stability during spinning.

5 Although fibrous fillers or non-fibrous fillers such as plate-like, scale-like, granular, irregular shaped or crushed fillers can be used for the filler, non-fibrous fillers are particularly preferable. Specific examples include potassium titanate whiskers, palladium titanate
10 whiskers, aluminum borate whiskers, silicon nitride whiskers, mica, talc, kaolin, silica, calcium carbonate, glass beads, glass flakes, glass microballoons, clay, molybdenum disulfide, wollastonite, titanium dioxide, zinc oxide, calcium polyphosphate, graphite, metal
15 powder, metal flakes, metal ribbon, metal oxides, carbon powder, black lead, carbon flakes and scaly carbon. Moreover, in the case the monofilament fineness of the wholly aromatic polyamide fibers is large, glass fibers, carbon fibers such as PAN and pitch fibers, metal fibers
20 such as stainless steel fibers, aluminum fibers or brass fibers, organic fibers such as wholly aromatic polyamide fibers, gypsum fibers, ceramic fibers, asbestos fibers, zirconia fibers, alumina fibers, silica fibers, titanium dioxide fibers, silicon carbide fibers, rock wool or
25 metal ribbon can be used. Two or more types of these fillers may also be used in combination.

Furthermore, the aforementioned fillers can also be used after treating the surface thereof with a known coupling agent (such as a silane-based coupling agent or
30 titanate-based coupling agent) or other surface treatment agent.

In the wholly aromatic polyamide fibers of the present invention, it is necessary that the layer-structured clay mineral be contained within the range of
35 0.05 to 20 parts by weight, preferably 0.1 to 10 parts by weight, and more preferably 0.5 to 5 parts by weight, relative to 100 parts by weight of the wholly aromatic

polyamide. If the content of layer-structured clay mineral is less than 0.05 parts by weight relative to 100 parts by weight of said wholly aromatic polyamide, improvement of toughness factor is not observed, while if
5 the content exceeds 20 parts by weight, the transparency of the spinning liquid composed of the layer-structured clay mineral, wholly aromatic polyamide and solvent becomes low and moldability decreases thereby making this undesirable.

10 In addition, if the degree of orientation A of the layer-structured clay mineral in the fibers is 50% or more, preferably 70% or more and more preferably 80% or more, mechanical properties (toughness factor) and various physical properties such as thermal dimensional
15 stability are improved, thereby making this preferable. Furthermore, the degree of orientation A of the layer-structured clay mineral particles is determined according to the following formula from the intensity distribution measured along a Debye ring of a reflection peak in a
20 (001) plane of the layer-structured clay mineral particles measured by X-ray analysis.

$$A = (180 - w) / 180 \times 100$$

In this formula, w represents the half value width (degrees) of an intensity distribution measured along a
25 Debye ring of a reflection peak.

The wholly aromatic polyamide fibers of the present invention preferably have a tensile strength that is 10% or more better, and an ultimate elongation (E) that is 10% or more better, than comparative wholly aromatic
30 polyamide fibers that are completely identical to the aforementioned wholly aromatic polyamide fibers with the exception of not containing a layer-structured clay mineral. Moreover, the wholly aromatic polyamide fibers of the present invention have a toughness factor (TF)
35 that is 10% or more better, particularly 20% or more better, and preferably 30% or more better than the comparative wholly aromatic polyamide fibers.

Furthermore, the toughness factor (TF) referred to here is defined as the product of tensile strength (T') as measured in units of grams/denier and ultimate elongation (E) as measured in units of percent, namely $T' \times (E)^{1/2}$.

5 If toughness factor is improved by 30% or more in this manner, as the strength of the fibers is improved, there is less filament breakage in the fibers even if the draw ratio is increased (improved quality), and retention of monofilaments on a drawing roller and so forth during
10 drawing decreases (improved process stability). In particular, an improvement of the toughness factor of 10% or more is preferable since stabilization effects in the drawing process become large.

 Moreover, the wholly aromatic polyamide fibers of
15 the present invention may also contain other additives such as antioxidants, heat stabilizers, weather resistance agents, dyes, antistatic agents, flame retardants or electrical conductivity agents within a range that does not impair the effects of the present
20 invention.

 The wholly aromatic polyamide fibers of the present invention can be produced by, for example, a process like that described below. Namely, the wholly aromatic polyamide fibers of the present invention can be produced
25 by a process comprising the steps of: (1) preparing a spinning liquid (dope) composed of wholly aromatic polyamide, layer-structured clay mineral and solvent, (2) coagulating the spinning liquid by introducing streams of the spinning liquid into an aqueous coagulation bath, (3)
30 drawing the coagulated filaments in a wetted atmosphere, and (4) dry-heat treating the drawn filaments.

 The blending ratio of the layer-structured clay mineral to the wholly aromatic polyamide in the spinning liquid is controlled to within the range of 0.05 to 20
35 parts by weight, preferably 0.1 to 10 parts by weight, and particularly preferably 0.5 to 5 parts by weight with respect to 100 parts by weight of the wholly aromatic

polyamide. In addition, the polymer concentration in the spinning liquid is preferably 0.1 to 30% by weight, more preferably 1 to 25% by weight, and even more preferably 15 to 25% by weight. Moreover, the haze of the spinning liquid is preferably adjusted to 10 or less and more preferably to 5 or less.

Furthermore, there are no limitations on the process used to prepare the spinning liquid. Examples of processes that can be used include: (A) a process in which the layer-structured clay mineral is added to a solution of the wholly aromatic polyamide, (B) a process in which a solution of the wholly aromatic polyamide and a dispersion of the layer-structured clay mineral are mixed with each other, and (C) a process in which the wholly aromatic polyamide is added to a solution of the layer-structured clay mineral.

When preparing the spinning liquid from the wholly aromatic polyamide polymer, layer-structured clay mineral particles and a solvent, the spinning liquid used in the present invention is preferably prepared by preparing a solution A, comprising a portion of the solvent, a portion of the wholly aromatic polyamide polymer, and 30 to 300 parts by weight of the layer-structured clay mineral particles relative to 100 parts by weight of this wholly aromatic polyamide polymer, separately preparing a solution B, comprising the remainder of the solvent and the remainder of the wholly aromatic polyamide polymer, and mixing solution A and solution B, such that the solvent A and the solvent B satisfy the following conditions at that time:

- (1) the viscosity of the solution A at a shear rate of 0.1 second^{-1} is 15 to 80 times the viscosity thereof at a shear rate of 10 second^{-1} ; and,
- (2) the viscosity of the solution A at a shear rate of 0.1 second^{-1} is 4 to 20 times the viscosity of solution at a shear rate of 0.1 second^{-1} .

As a result thereof, regions having a relatively

high density of layer-structured clay mineral particles can be uniformly dispersed and distributed in the spinning liquid which, together with stabilizing the spinning process, makes it possible to control the degree of dispersion Y of the layer-structured clay mineral particles in the resulting fibers to a desired value, thereby enhancing the effect of improving the toughness factor of the resulting fibers.

Here, if the ratio of the layer-structured clay mineral to the wholly aromatic polyamide in solution A is less than 30 parts by weight, the difference in viscosity with solution B decreases, the layer-structured clay mineral is more easily uniformly distributed in the resulting spinning liquid, and the effect of improving the toughness factor is reduced. On the other hand, if it exceeds 300 parts by weight, the distribution density of the layer-structured clay mineral becomes remarkably less uniform and, as a result, the stability of the spinning process may decrease.

In addition, if the viscosity of solution A at a shear rate of 0.1 second^{-1} is less than 4 times the viscosity of solution B at a shear rate of 0.1 second^{-1} , the layer-structured clay mineral is easily uniformly distributed, and as a result, the formation of regions having a comparatively large distribution density of layer-structured clay mineral particles decreases, and the effect of improving the toughness factor is reduced. On the other hand, if it exceeds 20 times, the formation of regions having a relatively high distribution density of layer-structured clay mineral particles in the spinning liquid during the spinning process becomes excessive, and as a result, increases in packing pressure and so forth occur, and process stability may decrease. Moreover, if the viscosity of solution A at a shear rate of 0.1 second^{-1} is less than 15 times the viscosity thereof at a shear rate of 10 second^{-1} , the layer-structured clay mineral is easily uniformly distributed

in the fibers and, as a result, the formation of regions having a comparatively large distribution density of layer-structured clay mineral particles decreases, and the effect of improving the toughness factor is reduced. On the other hand if it exceeds 20 times, the formation of regions having a relatively high distribution density of layer-structured clay mineral particles in the spinning liquid during the spinning process becomes excessive and, as a result, the process stability may decrease.

Although the solvent used to prepare the spinning liquid is arbitrary, provided it dissolves the wholly aromatic polyamide, those consisting primarily of an amide-based polar solvent are preferable, specific examples of which include aprotic amide-based organic solvents such as N-methyl-2-pyrrolidone (NMP), N-ethyl-2-pyrrolidone, N,N-dimethylacetamide, dimethylformamide, tetramethyl urea, hexamethylphosphoramide and N-methylbutyrolactam. Although the temperature of the spinning liquid should be suitably set according to the solubility of the wholly aromatic polyamide, it is preferable to set within the range of 50 to 90°C from the standpoint of spinability in the case of polymetaphenylene isophthalamide.

In the process of the present invention, filamentary streams of the spinning liquid are introduced, for example, directly into an aqueous coagulation bath from a spinneret normally having 10 to 30,000 discharge holes to coagulate the filamentary stream and form undrawn fibers. There are no particular limitations on the composition of the aqueous coagulation bath used here and, although the composition should be suitably selected according to the types of the wholly aromatic polyamide and solvent used, a conventionally known aqueous coagulation bath containing an inorganic salt and/or solvent can be used. More specifically, if the wholly aromatic polyamide is polymetaphenylene isophthalamide and the solvent is N-

methyl-2-pyrrolidone (NMP), a preferable example of the aqueous solution has a calcium chloride concentration of 34 to 42% by weight and an NMP concentration of 3 to 10% by weight. In this case, the temperature of the aqueous coagulation bath is suitably within a range of 80 to 95°C, the immersion time of the fibers in the coagulation bath is suitably within the range of 1 to 11 seconds.

Since a considerable amount of solvent remains on the undrawn fibers removed from the coagulation bath, the undrawn fibers are preferably washed to extract and remove the residual solvent. Examples of methods that are employed include passing the undrawn fibers through a water bath after having removed them from the coagulation bath, and spraying water onto the undrawn fibers. The solvent content in the fibers after washing is preferably controlled to 30% by weight or less, and if this content is exceeded, water may penetrate into the fibers in the next drawing process or voids may be easily formed resulting in decreased fiber strength.

The washed undrawn fibers are drawn in a wetted atmosphere, and preferably in a warm water bath while, simultaneously, residual solvent and inorganic salts such as calcium chloride used in combination as necessary, are removed by washing. The drawing temperature during the aforementioned drawing is suitably set according to the amount of solvent remaining in the undrawn fibers. For example, in the case the amount of residual solvent is 50% or more relative to the polymer weight, the drawing temperature is preferably controlled to 0 to 50°C, while in the case the amount of residual solvent is less than 50% relative to the polymer weight, the drawing temperature is preferably controlled to 50 to 100°C. In addition, the draw ratio is preferably controlled to 1.05 times or more, more preferably 1.10 times or more and even more preferably 0.3 to 0.6 times the maximum draw ratio of the undrawn fibers (draw ratio at which filament

breakage begins to occur when drawn under identical conditions).

5 The resulting drawn fibers are normally dried at a temperature of 100°C or higher followed by hot drawing as necessary and subsequent heat treatment using a heating roller or heating plate.

10 Wholly aromatic polyamide fibers obtained in this manner are then housed in a drum as necessary, coiled or sent directly to post-processing, or after crimping as necessary, are cut and supplied to any subsequent desired process as short fibers.

EXAMPLES

15 The following provides a more detailed explanation of the present invention through examples thereof.

In the examples, the specific properties were measured by the following tests.

(Intrinsic Viscosity IV)

20 A test polymer was dissolved in NMP at a concentration of 0.5 g/100 ml, and the viscosity of this solution was measured at 30°C using an Ostwald viscometer, after which intrinsic viscosity was calculated from this measured value.

(Viscosity)

25 The viscosity of the spinning liquid was measured at 70°C using a viscometer manufactured by Rheometric Scientific (trade name: Rheomat 115).

(Fineness)

Fineness was measured in compliance with JIS-L-1015.

(Tensile Strength, Ultimate Elongation)

30 Tensile strength and ultimate elongation were measured in compliance with JIS-L-1015 using a sample length of 20 mm, initial load of 0.05 g/dtex and drawing speed of 20 mm/min.

(Layer-structured Clay Mineral Degree of Orientation

35 A)

The degree of orientation was measured using an X-

ray generator (Rigaku Denki, RU-200B) under conditions of CuK α rays for the target, voltage of 45 kV and current of 70 mA. The incident X-rays were converged and converted to monochromatic rays with a multilayer-structured mirror manufactured by Osmic followed by measurement of the fiber sample using the vertical transmission method. Detection of refracted X-rays was measured using an imaging plate (Fuji Photo Film) measuring 200 mm $\times$ 250 mm under conditions of a camera length of 250 mm. The degree of orientation of the clay layer surface was determined with the following formula from the intensity distribution measured along a Debye ring of a reflection peak in a (001) plane.

$$A = (180 - w)/180 \times 100$$

In this formula, w represents the half width value of the intensity distribution measured along a Debye ring of the reflection peak.

(Spinning Liquid Haze)

The haze of the spinning liquid filled into a cell having an optical path length of 1 cm was measured using the NDH2000 Turbidity Meter manufactured by Nippon Denshoku.

(Average Layer Thickness of Layer-structured Clay Mineral Particles)

The layer thicknesses of all layer-structured clay mineral particles observed in a cross-sectional area measuring 25 μm^2 in a transmitting electron micrograph (TEM, magnification: 100,000x) of a fiber longitudinal cross-section measured using the H-800 Electron Microscope manufactured by Hitachi, Ltd., followed by calculation of their average value.

(Degree of Dispersion (Y) of Layer-structured Clay Mineral)

The aforementioned wholly aromatic polyamide fibers were cut along the fiber axis, and the resulting longitudinal cross-sections were observed at a

magnification of 100,000x with a transmitting electron microscope (Model H-800) manufactured by Hitachi, Ltd.. When the total surface area S1 of a plurality of regions in which changes in the state of the fiber cross-sections were observed due to the effects of the aforementioned layer-structured clay mineral particles per 25 μm^2 of the observed cross-sectional area S2 was measured, the degree of dispersion Y of the layer-structured clay mineral particles in the fibers as defined by the aforementioned formula (1) was calculated according to the following formula.

$$Y (\%) = (S1/S2) \times 100$$

The average value of Y was determined from three measurements.

(Solution Shear Viscosity)

The shear viscosity of the solution when preparing the spinning liquid was measured at a temperature of 70°C using the Rheomat 115 manufactured by Rheometric Scientific.

(Fiber Solvent Content N)

The fibers were centrifuged for 10 minutes (rotating speed: 5000 rpm) prior to drawing and then boiled for 4 hours in methanol to extract the solvent and water in the fibers. The weight of the methanol solution M2 after extraction and the dry weight of the fibers M1 were measured and the solvent weight concentration C (%) in the extract was determined with a gas chromatograph followed by calculation of the solvent content N according to the following formula.

$$N = (C/100 \times M2)/M1 \times 100$$

(Filament Breakage)

A plurality of the resulting drawn fibers were uniformly formed into a fiber bundle, one end of the fiber bundle was immobilized and then the bundle was cut so that the length to the other end, from the immobilized end, was 20 cm. The total number of filaments of the

fiber bundle at this time was designated as H. Next, the fiber bundle was moved back and forth 10 times in the longitudinal direction in a bath filled with water (longitudinal width: 0.5 m), after which the fiber bundle was taken out followed by counting the number of filaments that remained in the bath. This procedure was repeated five times and the total number of filaments that remained in the bath was designated as M. The number of broken filaments in 15000 m (X) was then calculated using the formula below and this was repeated three times to determine the average value.

$$X = M \times 15000 / (H \times T \times 0.2)$$

Example 1

215 g of polymetaphenylene isophthalamide having an intrinsic viscosity of 1.35 dl/g were dissolved in 785 g of NMP and stirred to a uniformly transparent dope. Separate from this procedure, a layer-structured clay mineral in the form of a smectite clay mineral treated with polyoxypropylene methyl diethyl ammonium chloride (trade name: Lucentite SPN, Co-op Chemical) was mixed and dispersed in NMP to a concentration of 1% by weight. The resulting layer-structured clay mineral dispersion was added to the wholly aromatic polyamide solution so as to have the composition shown in Table 1 followed by stirring to prepare a spinning liquid (dope). The haze of the resulting dope was 2.41. After degassing the resulting dope, it was extruded into the shape of filamentary streams from a spinneret having a cap diameter of 0.07 mm and 100 holes, the filamentary streams were introduced into a coagulation bath composed of a 43% aqueous calcium chloride solution (containing 1% by weight NMP) at 85°C, and then coagulated at a spinning speed of 7 m/min. After washing, the resulting undrawn fibers were drawn to 2.4 times in boiling water followed by drying at 120°C and then subjecting to drawing heat setting by 1.75 times at 350°C to obtain wholly aromatic

polyamide fibers containing a layer-structured clay mineral. Measurement of the longitudinal cross-section of the filaments by TEM demonstrated that the average layer thickness of the layer-structured clay mineral particles was 90 nm. In addition, the degree of orientation A of the layer-structured clay mineral particles as obtained from the results of X-ray diffraction was 91%. The tensile strength, ultimate elongation and toughness factor (TF) of the resulting fibers are shown in Table 1.

Example 2

Wholly aromatic polyamide fibers having the composition shown in Table 1 were produced in the same manner as Example 1 with the exception that smectite layer-structured clay mineral (trade name: Lucentite STN, Co-op Chemical) treated with trioctyl methyl ammonium chloride was used for the layer-structured clay mineral. The haze of the spinning liquid at this time was 1.92. In addition, the average layer thickness of the layer-structured clay mineral particles was 86 nm, and the degree of orientation A was 91%. The tensile strength, ultimate elongation and toughness factor (TF) of the resulting fibers are shown in Table 1.

Comparative Example 1

Wholly aromatic polyamide fibers were produced in the same manner as Example 1 with the exception of not containing layer-structured clay mineral. The tensile strength, ultimate elongation and toughness factor (TF) of the resulting fibers are shown in Table 1.

Table 1

	Amt. of layer- structured clay mineral added (wt%)	Filament fineness (dtex)	Degree of orientation A of layer- structured clay mineral particles (%)	Tensile strength (cN/dtex)	Ultimate elongation (%)	Toughness factor
Ex. 1	2.0	1.74	91	4.42	40.7	32
Ex. 2	1.0	1.21	91	5.56	28.9	34
Comp. Ex. 1	0	2.26	--	3.89	29.5	24

Example 3

0.16 parts by weight of polymetaphenylene
 5 isophthalamide having an intrinsic viscosity of 1.9 dl/g
 were dissolved in 1.46 parts by weight of NMP and stirred
 to a uniformly transparent dope. 0.18 parts by weight of
 layer-structured clay mineral in the form of smectite
 clay mineral treated with polyoxypropylene methyl diethyl
 10 ammonium chloride (trade name: Lucentite SPN, Co-op
 Chemical) were added to this dope followed by stirring to
 prepare Polymer Solution A. Separate from this
 procedure, 17.44 parts by weight of polymetaphenylene
 isophthalamide were dissolved in 63.68 parts by weight of
 15 NMP to prepare transparent Polymer Solution B.

After mixing and stirring the Polymer Solutions A
 and B, 17.08 parts by weight of NMP were further added to
 this mixture to prepare a spinning liquid composed of
 17.60 parts by weight of polymetaphenylene
 20 isophthalamide, 0.18 parts by weight of Lucentite SPN
 (trade name) and 82.22 parts by weight of NMP.

This spinning liquid was heated to 85°C and extruded
 in the form of a filament stream from a spinneret having
 a hole diameter of 0.07 mm and 1500 holes and then
 25 introduced into a coagulation bath at 85°C to prepare
 undrawn fibers. The composition of the coagulation bath
 consisted of 40% by weight of calcium chloride, 5% by
 weight of NMP and 55% by weight of water, and the
 immersion length (effective coagulation bath length) was

100 cm. After passing the undrawn fibers through the coagulation bath at a speed of 7.0 m/min, the fibers were temporarily pulled out of the bath into air. The coagulated undrawn filaments were sequentially washed in first through third aqueous washing baths. The total immersion time of this washing was 50 seconds. Furthermore, water at a temperature of 30°C was used for the first through third washing baths. Next, the washed and undrawn filaments were drawn 2.4 times in hot water at 95°C, and after washing by continuing to immerse for 48 seconds in hot water at 95°C, the filaments were dry-heat treated by winding onto a roller having a surface temperature of 130°C. Subsequently, the filaments were drawn 1.75 times while contacting with a heating plate having a surface temperature of 330°C to produce polymetaphenylene isophthalamide fibers. The fineness of these fibers was 2.26 dtex, the tensile strength was 5.16 cN/dtex, and the ultimate elongation was 43.2%.

The maximum draw ratio in the above-mentioned was 4.7 (draw ratio/maximum draw ratio = 0.51), k and the solvent content before drawing was 5.0 parts by weight relative to 100 parts by weight of the wholly aromatic polyamide.

In addition, the number of broken filaments in the above-mentioned spinning and drawing processes were 6 per length of 15000 m, and the degree of dispersion Y of the layer-structured clay mineral was 3%. The test results are shown in Table 2.

Example 4

0.32 parts by weight of the same polymetaphenylene isophthalamide powder used in Example 3 were dissolved in 6.46 parts by weight of NMP cooled to -10°C to prepare a transparent polymer solution. 0.72 parts by weight of layer-structured clay mineral in the form of smectite clay mineral (trade name: Lucentite SPN, Co-op Chemical) were added thereto followed by stirring to prepare

Polymer Solution A. Separate from this procedure, 13.28 parts by weight of polymetaphenylene isophthalamide were dissolved in 48.49 parts by weight of NMP cooled to -10°C to prepare transparent Polymer Solution B.

5 After mixing and stirring the Polymer Solutions A and B, 30.73 parts by weight of NMP were further added to this mixture to obtain a spinning liquid composed of 17.60 parts by weight of polymetaphenylene isophthalamide, 6.80 parts by weight of Lucentite SPN
10 (trade name) and 76.6 parts by weight of NMP.

 This spinning liquid was spun and drawn according to the same conditions and procedure as Example 3 to produce polymetaphenylene isophthalamide fibers having fineness of 2.18 dtex, tensile strength of 6.03 cN/dtex, and
15 ultimate elongation of 45.3%.

 The number of broken filaments in the above-mentioned spinning and drawing processes were 10 per length of 15000 m, and the degree of dispersion Y of the layer-structured clay mineral was 25%. The test results
20 are shown in Table 2.

Table 2

		Example 3	Example 4
Layer-structured clay mineral	wt%*	1.0	4.0
Solution A viscosity:			
Shear viscosity: 0.1 sec^{-1}	(poise)	2730	3420
Shear viscosity: 10 sec^{-1}	(poise)	90	95
Solution B viscosity:			
Shear viscosity: 0.1 sec^{-1}	(poise)	420	410
Fineness	(dtex)	2.26	2.18
Tensile strength	(cN/dtex)	5.17	5.32
Ultimate elongation	%	43.2	45.3
Toughness factor (TF)		38.5	40.6
Filament breakage	(no./15000 m)	6	10
Degree of dispersion Y	(%)	3	25

*: Based on weight of wholly aromatic polyamide.

Example 5

25 Spinning and drawing were carried out according to the same conditions and procedure as Example 3. However, although the same spinning solution as Example 3 was used, the hot water draw ratio was 2.8 times, and the hot

plate draw ratio at 330°C was 1.50 times.

Polymetaphenylene isophthalamide fibers were obtained that had a filament fineness of 2.22 dtex, tensile strength of 5.49 cN/dtex and ultimate elongation of 40.7%.

The maximum draw ratio in the hot water drawing process was 4.7 (draw ratio/maximum draw ratio = 0.60), and the solvent content of the fibers prior to drawing was 5.0 parts by weight relative to 100 parts by weight of the wholly aromatic polyamide.

In addition, the number of broken filaments in the fibers was 8 per 15000 m. The test results are shown in Table 3.

Example 6

Spinning and drawing were carried out according to the same conditions and procedure as Example 3. However, although the same spinning solution as Example 3 was used, the washing time prior to hot water drawing was 34 seconds. Fibers were obtained that had a filament fineness of 2.21 dtex, tensile strength of 6.12 cN/dtex and ultimate elongation of 48.3%.

The maximum draw ratio in the hot water drawing process was 4.9 (draw ratio/maximum draw ratio = 0.49), and the solvent content of the fibers prior to drawing was 14.0 parts by weight relative to 100 parts by weight of the wholly aromatic polyamide.

In addition, the number of broken filaments in the fibers was 2 per 15000 m. The test results are shown in Table 3.

Table 3

		Example 3	Example 5	Example 6
Layer-structured clay mineral	wt%*	1.0	1.0	1.0
NMP content in undrawn fibers	ppw*	5.0	5.0	14.0
Maximum draw ratio		4.7	4.7	4.9
Draw ratio		2.4	2.8	2.4
Draw ratio/max. draw ratio	Ratio	0.51	0.60	0.49
Filament fineness	(dtex)	2.26	2.22	2.21
Tensile strength	(cN/dtex)	5.16	5.49	6.12
Elongation	(%)	43.2	40.7	48.3
Filament breakage	(No./15000 m)	6	8	2

*: Based on weight of wholly aromatic polyamide

5 **: Content per 100 parts by weight of wholly aromatic polyamide

INDUSTRIAL APPLICABILITY

As wholly aromatic polyamide fibers of the present invention have improved mechanical strength, degree of elongation and toughness factor as compared with fibers
10 of the prior art not containing a layer-structured clay mineral, they can be used in various applications that take advantage of these characteristics. In addition, according to the production process of the present invention, the occurrence of filament breakage during
15 spinning and drawing can be reduced, and fibers of stable quality can be stably produced industrially.

CLAIMS

1. Drawn and oriented wholly aromatic polyamide fibers comprising a resin composition comprising a matrix composed of a wholly aromatic polyamide resin and layer-structured clay mineral particles dispersed and distributed in an amount of 0.05 to 20 parts by mass, based on 100 parts by mass of the matrix, in the matrix.

2. The wholly aromatic polyamide fibers as claimed in claim 1, wherein a plurality of regions, in which the layer-structured clay mineral particles are distributed in a relatively high distribution density, are scatteringly distributed in the wholly aromatic polyamide matrix.

3. The wholly aromatic polyamide fibers as claimed in claim 1 or 2, wherein when the wholly aromatic polyamide fibers are cross-cut along the fiber axes, the resultant cross-sectional profiles are observed with an electronic microscope at a magnification of 100,000, and in each cross-sectional profile, a total area S1 of a plurality of regions in which regions a change in conditions of the fiber cross-sectional profile due to an influence of the layer-structured clay mineral particles distributed in the observation area S2 of $25 \mu\text{m}^2$ is found, is measured, the degree of dispersion Y of the layer-structured clay mineral particles in each fiber, defined by the equation (1):

$$Y(\%) = (S1/S2) \times 100 \quad (1)$$

is in the range of from 0.1 to 40.

4. The wholly aromatic polyamide fibers as claimed in any one of claims 1 to 3, wherein the layer-structured clay mineral comprises at least one selected from hectorite, saponite, stevensite, beidellite, montmorillonite and swelling mica.

5. The wholly aromatic polyamide fibers as claimed in any one of claims 1 to 3, wherein the layer-structured clay mineral particles are ones treated with an intercalating agent.

6. The wholly aromatic polyamide fibers as claimed in any one of claims 1 to 3, wherein the layer-structured clay mineral particles have an average layer thickness of 10 to 500 nm.

5 7. The wholly aromatic polyamide fibers as claimed in any one of claims 1 to 3, wherein the layer-structured clay mineral particles have a degree of orientation A of 50% or more, determined in accordance with the equation (2):

10
$$A(\%) = [(180 - w)/180] \times 100 \quad (2)$$

In equation (2), w represents a half value width of an intensity distribution determined, in an X-ray analysis of the layer-structured clay mineral particles, along a Debye ring of a reflection peak in a
15 (001) plane of the layer-structured clay mineral particles.

8. The wholly aromatic polyamide fibers as claimed in any one of claims 1 to 3, wherein a ratio (T/To) of a tensile strength (T) of the wholly aromatic polyamide
20 fibers to a tensile strength (To) of comparative wholly aromatic polyamide fibers identical to the wholly aromatic polyamide fibers except that the layer-structured clay mineral particles are not contained therein, is 1.1 or more.

25 9. The wholly aromatic polyamide fibers as claimed in any one of claims 1 to 3, wherein a ratio (E/Eo) of an ultimate elongation (E) of the wholly aromatic polyamide fibers to an ultimate elongation (Eo) of comparative wholly aromatic polyamide fibers identical to the wholly
30 aromatic polyamide fibers except that the layer-structured clay mineral particles are not contained therein, is 1.1 or more.

10. The wholly aromatic polyamide fibers as claimed in any one of claims 1 to 3, wherein the toughness factor
35 (TF) of the wholly aromatic polyamide fibers defined by the equation (3):

$$TF = T' \times E'^{1/2} \quad (3)$$

In which equation (3), T' represents a numeral value of the tensile strength in unit of g/1.1 dtex of the wholly aromatic polyamide fibers and E' represents a numeral value of the ultimate elongation in unit of % of the wholly aromatic polyamide fibers, is 30 or more.

11. The wholly aromatic polyamide fibers as claimed in claim 10, wherein the ratio (TF/TF_0) of the tenacity factor (TF) of the wholly aromatic polyamide fibers to the tenacity factor (TF_0) of comparative wholly aromatic polyamide fibers identical to the wholly aromatic polyamide fibers except that the layer-structured clay mineral particles are not contained therein, is 1.1 or more.

12. The wholly aromatic polyamide fibers as claimed in any one of claims 1 to 3, wherein the layer-structured clay mineral particles contain organic onium ions located between layers thereof.

13. The wholly aromatic polyamide fibers as claimed in any one of claims 1 to 3, wherein the wholly aromatic polyamide resin is selected from meta-wholly aromatic polyamide resins.

14. A process for producing drawn and oriented wholly aromatic polyamide fibers comprising extracting a spinning liquid comprising a solvent and a wholly aromatic polyamide resin and layer-structured clay mineral particles in an amount of 0.05 to 20 parts by mass per 100 parts by mass of the wholly aromatic polyamide resin through a spinneret to form filamentary streams of the spinning liquid;

Introducing the filamentary streams of the spinning liquid into an aqueous coagulation bath to coagulate the filamentary streams of the spinning liquid;

drawing the resultant undrawn filaments in a wetted atmosphere; and

dry-heat treating the resultant drawn filaments.

15. The process for producing wholly aromatic

polyamide fibers as claimed in claim 14, wherein the spinning liquid is prepared by mixing a solution A comprising a portion of the solvent, a portion of the wholly aromatic polyamide resin and layer-structured clay mineral particles in an amount of 30 to 300 parts by mass per 100 parts by mass of the wholly aromatic polyamide resin with a solution B comprising the remaining portion of the solvent, the remaining portion of the wholly aromatic polyamide resin, and satisfies the requirements (1) and (2):

(1) the viscosity of the solution (A) at a shear rate of 0.1 second^{-1} is 15 to 80 times the viscosity thereof at a shear rate of 10 second^{-1} , and

(2) the viscosity of the solution (A) at a shear rate of 0.1 second^{-1} is 40 to 20 times the viscosity of the solution (B) at a shear rate of 0.1 second^{-1} .

16. The process for producing wholly aromatic polyamide fibers as claimed in claim 14 or 15, wherein the concentration of the wholly aromatic polyamide resin in the spinning solution is 0.1 to 30% by mass.

17. The process for producing wholly aromatic polyamide fibers as claimed in claim 14 or 15, wherein the draw ratio of the undrawn filaments in the wetted atmosphere is in the range of 0.3 to 0.6 times the maximum draw ratio of the undrawn filaments.

18. The process for producing wholly aromatic polyamide fibers as claimed in claim 14 or 15, wherein the solvent is selected from polar amide solvents.

19. The process for producing wholly aromatic polyamide fibers as claimed in claim 14 or 15, wherein the wholly aromatic polyamide resin is selected from meta-wholly aromatic polyamide resins.