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(54) Title: MODIFIED FIBER AND PREPARATION METHOD THEREFOR

(57) **Abrégé/Abstract:**

Modified fiber and a preparation method therefor. By means of a physical method, uniform dispersion of graphite particles in a polyester base material and a polyamide base material is realized, the technology is simple, a dispersing agent is not needed, and industrial production is easy. By introducing graphene into hollow cotton or polyamide fiber, and particularly introducing biomass graphene into the hollow cotton or polyamide fiber, modified hollow cotton or polyamide fiber is enabled to have a low-temperature far infrared function, the far infrared normal emittance thereof being not less than 0.85; the antibacterial performance is greater than 90%; and the heat preservation performance and the air permeability are both remarkable, and when the content of the biomass graphene is 1.4%, the heat preservation rate is equal to that of white duck down and is about 90%, but the air permeability is about 240 mm/s and is far higher than that of the duck down.

Abstract

Modified fiber and a preparation method therefor. By means of a physical method, uniform dispersion of graphite particles in a polyester base material and a polyamide base material is realized, the technology is simple, a dispersing agent is not needed, and industrial production is easy. By introducing graphene into hollow cotton or polyamide fiber, and particularly introducing biomass graphene into the hollow cotton or polyamide fiber, modified hollow cotton or polyamide fiber is enabled to have a low-temperature far infrared function, the far infrared normal emittance thereof being not less than 0.85; the antibacterial performance is greater than 90%; and the heat preservation performance and the air permeability are both remarkable, and when the content of the biomass graphene is 1.4%, the heat preservation rate is equal to that of white duck down and is about 90%, but the air permeability is about 240 mm/s and is far higher than that of the duck down.

MODIFIED FIBER AND PREPARATION METHOD THEREFOR

Technical field

The present disclosure belongs to the field of fiber preparation, and in particular relates to a modified fiber and a preparation method thereof. The modified fiber includes modified hollow cotton or modified polyamide fiber.

Background

Polyester is an important type of synthetic fibers, and it is the trade name of polyester fiber in China, and is a fiber made of polyethylene terephthalate (PET) or polybutylene terephthalate (PBT) through spinning and post-processing.

Polyethylene terephthalate (PET) is a fiber-forming polymer made by using poly-terephthalic acid (PTA) or dimethyl terephthalate (DMT) and ethylene glycol (EG) as raw materials through esterification or transesterification and polycondensation. Polybutylene terephthalate (PBT) is a fiber-forming polymer made by using poly-terephthalic acid (PTA) or dimethyl terephthalate (DMT) and 1,4-butylene glycol as raw materials through esterification or transesterification and polycondensation.

Polyester is the one made by the simplest process among the three major synthetic fibers, and it is relatively inexpensive, and is well-popularized due to its characteristics such as durability, good elasticity, non-easy deformability, corrosion resistance, insulation, stiff and smooth, and easy rinsibility and quick drying, etc.

Polyester hollow cotton is made of different specifications of polyester superfine fibers through special process. Since its texture resembles down feather, polyester hollow cotton is also called as silk wadding or down cotton, and is widely used in various warmth retention products such as down coats, down trousers, ski shirts, cotton wadded jackets, down quilts, and seat cushions, etc. The disadvantage of existing polyester hollow cotton is that it has less warmth retention property, is not water washable, and is not lightweight.

Polyamide, i.e., polyamide fiber, commonly known as Nylon, which has an English name of Polyamide (abbreviated as PA), with a density of about 1.15 g/cm^3, is a generic name of thermoplastic resins containing repeating amide group -NHCO- in the main chain of the molecule, including aliphatic PA, aliphatic-aromatic PA and aromatic PA. Among them, there are many types of aliphatic PAs, which have large yields and are widely used. The nomenclature is determined by the specific number of carbon atoms in the monomers for synthesis.

The most outstanding advantage of polyamide is that its abrasion resistance is higher than that of all other fibers. Its abrasion resistance is 10 times higher than that of cotton and 20 times higher than that of wool. Adding some polyamide to blended fabrics can greatly increase the abrasion resistance. When stretched up to 3-6%, the elastic recovery rate can reach 100%, and the blended fabrics can withstand tens of thousands of times of rupture without breaking. The strength of polyamide fiber is 1-2 times higher than that of cotton, 4-5 times higher than that of wool, and 3 times of viscose fiber.

However, polyamide has no thermal insulation property. When it is used as fabrics such as socks and clothes, the thermal insulation effect thereof is poor, which is especially prone to cause problems such as joint pain, etc. For socks or intimates, body scurf is easily left thereon, breeding bacteria and causing odors.

Therefore, there is a need to develop a functional modified polyamide fiber.

Graphene is a two-dimensional crystal stripped from graphite material, consisting of carbon atoms, and only having one-layer-atom thick, and is a novel nano-material that has been found currently to be the thinnest, have maximal strength and maximal electrical and thermal conductivities. The addition of graphene to a substrate such as polyester or polyamide is expected to give new properties to polyester or polyamide, especially the addition of biomass graphene with bacteria inhibition and low-temperature far infrared functions, the polyester or polyamide is expected to have bacteria inhibition and low-temperature far infrared functions.

However, the solid state of graphene is easy to agglomerate to form larger particle agglomerates, and when it is added to a substrate such as polyester or polyamide, it is not easily dispersed uniformly, which greatly reduces the processing fluidity of substrate masterbatches such as polyester or polyamide, and thus the spinning process cannot be performed. Therefore, graphene cannot be applied in a substrate material such as polyester or polyamide.

In the related technologies, in order to uniformly disperse graphene, a dispersing agent is often added, but the dispersing agent has a degrading effect on the materials. Therefore, it is an urgent issue needed to be solved in the art that how to find a method for uniformly doping graphene into a substrate such as polyester or polyamide without adding a dispersing agent, so that the properties of graphene (e.g., thermal insulation property, low-temperature far-infrared and bacteria inhibition property) can be fully used.

Summary

In view of the technical problem of the related technologies, i.e., graphene cannot be doped into fiber materials (including polyester and polyamide materials) without using a dispersing agent to obtain a modified hollow cotton or a modified polyamide fiber having thermal insulation property, low-temperature far-infrared and bacteria inhibition properties, the object of the present disclosure is to provide a modified hollow cotton, which is doped with graphene.

The “modified hollow cotton” of the present disclosure is obtained by doping with graphene, and it can also be called by a person skilled in the art as hollow cotton blend, hollow cotton composite, hollow cotton modifier, graphene-containing hollow cotton or graphene-containing modified hollow cotton.

The term “doping” used in the present disclosure means that graphene is added to the hollow cotton in various forms that can be conceived by those skilled in the art. Typical but non-limiting examples may be dispersing graphene on the surface of the hollow cotton, or in situ compositing graphene with the substrate of the modified hollow cotton, or physically blending graphene with the hollow cotton. “Doping” can also be replaced with “containing”, “comprising”, “dispersing” and “having”, etc., by those skilled in the art.

The so-called “hollow cotton” is a bat wool product with high warmth retention property with the fiber material being polyester.

Preferably, the graphene is a biomass graphene.

The biomass graphene is prepared from biomass; preferably, the biomass graphene is prepared from biomass-derived cellulose.

Carbon six-membered ring honeycomb lamellar structures having more than 10 layers and a thickness of 100 nm or less are called graphene nanosheets; carbon six-membered ring honeycomb lamellar structures having more than 10 layers and a thickness of 100 nm or less and prepared by using biomass as carbon source are called biomass graphene nanosheets; carbon six-membered ring honeycomb lamellar structures having 1-10 layers are called graphene; and carbon six-membered ring honeycomb lamellar structures having 1-10 layers and prepared by using biomass as carbon source are called biomass graphene.

The graphene of the present disclosure includes graphene nanosheet layer and graphene, and further includes biomass graphene nanosheet layer and biomass graphene.

The graphene of the present disclosure can be obtained by different preparation methods, for example mechanical exfoliation method, epitaxial growth method, chemical vapor deposition method, and graphite oxidation-reduction method, and it can also be graphene prepared through hydrothermal carbonization of biomass resources, and other methods in the related technologies. However, no matter which method is used, it is difficult to achieve large-scale production of graphene strictly theoretically. For example, certain impurity elements, and other allotropes of carbon element or graphene structures with non-single-layer or even multi-layer (e.g., 3 layers, 5 layers, 10 layers, and 20 layers, etc.) will present in the graphene prepared in the related technologies, and graphene used in the present disclosure also includes nonstrictly theoretically graphene described above.

Preferably, the biomass is any one selected from the group consisting of agricultural and forestry wastes, plants, and a combination of at least two selected therefrom.

Preferably, the plants are any one selected from the group consisting of coniferous wood, broadleaf wood, and a combination of at least two selected therefrom.

Preferably, the agricultural and forestry wastes are any one selected from the group consisting of corn stalks, corn cobs, sorghum stalks, beet residues, bagasse, furfural residues, xylose residues, wood chips, cotton stalks, shells, reeds, and a combination of at least two selected therefrom.

Preferably, the agricultural and forestry wastes are corn cobs.

In addition to the above list of biomass, the biomass according to the present disclosure may be any one of biomass resources that can be known by those skilled in the art, which will not be repeated herein.

The biomass graphene of the present disclosure refers to graphene prepared by using biomass as carbon source. specific processes for preparing graphene using biomass as carbon source have been reported in the art. Typical but non-limiting examples include CN104724699A, which will not be repeated herein.

For the biomass graphene, a typical but non-limiting example may be any one selected from the group consisting of substance ①, substance ②, substance ③, substance ④ having the properties described in Table a, and a combination of at least two:

Table a

Items	Performance indicators			
	Substance ①	Substance ②	Substance ③	Substance ④
Conductivity, S/m	2800-8000	5000-8000	2800-4000	3000-8000
Specific surface area, m^2/g	⩾150	⩾150	⩾300	⩾250
Raman spectrum, IG/ID	⩾2.0	⩾3.0	⩾2.0	⩾2.0
C/O	⩾35.0	⩾40.0	⩾35.0	⩾40.0
Ash content, %	1.0-4.0	2.0-4.0	1.0-2.5	1.0-2.0
Fe, %	0.1-0.5	0.1-0.5	0.1-0.5	0.1-0.5
Si, %	0.05-0.3	0.05-0.3	0.05-0.3	0.05-0.3
Al, %	0.05-0.4	0.05-0.4	0.05-0.4	0.05-0.4

In Table a, IG/ID is the peak height ratio of G peak to D peak in the Raman spectrum.

The biomass graphene of the present disclosure has a peak height ratio of the G peak to D peak of preferably 2.0 or more, further preferably 3.0 or more, and particularly preferably 5.0 or more. Optionally, the biomass graphene of the present disclosure has a peak height ratio of the G peak to D peak of 30 or less, for example, 27, 25, 20, 18, 15, 12, 10, 8, and 7, etc.

Those skilled in the art should understand that the performance indicators of the biomass graphene listed in Table a all refer to the indicators of the powder of the biomass graphene. If the biomass graphene is slurry, the above indicators are the indicators of the powder before preparing the slurry.

When the biomass graphene is powder, the biomass graphene has the following properties in addition to the performance indicators described in Table a:

black powder, uniform fineness, no significant large particles, a water content of 3.0% or less, a particle size D90 of 10.0 μm or less, a pH of 5.0 to 8.0, and an apparent density of 0.2 to 0.4 g/cm^3.

When the biomass graphene is a slurry, it is a product obtained by dispersing biomass graphene in a solvent, and the biomass graphene has the following properties in addition to the performance indicators described in Table a:

a solid content of 1.0 to 10.0%, a particle size D50 of 0.7 μm or less, a pH of 8.0 to 10.0, a Zeta potential of -10 mV or less, and a viscosity of 5.0 to 8.0 mpa.s.

The biomass graphene belongs to carbon nanostructure-containing composite, and the carbon nanostructure-containing composite contains graphene, amorphous carbon and non-carbon non-oxygen elements; the non-carbon non-oxygen elements include elements of Fe, Si and Al; and the content of the non-carbon non-oxygen elements is 0.5 wt% to 6 wt% of the composite.

Preferably, the content of carbon element in the carbon nanostructure-containing composite is 80 wt% or more, for example 82 wt%, 86 wt%, 89 wt%, 91 wt%, 94 wt%, 97 wt%, and 99 wt%, etc., preferably 85 wt% to 97 wt%, more preferably 90 wt% to 95 wt%.

Preferably, the non-carbon non-oxygen elements account for 0.3 wt% to 5 wt% of the carbon nanostructure-containing composite, for example 0.7 wt%, 1.1 wt%, 1.3 wt%, 1.6 wt%, 2 wt%, 2.8 wt%, 3.5 wt%, 4.2 wt%, 5.3 wt% or 5.8 wt%, preferably 1.5 wt% to 5 wt%.

In the carbon nanostructure-containing composite of the present disclosure, the graphene structure preferably has a carbon six-membered ring honeycomb lamellar structure having a thickness of 100 nm or less, preferably a carbon six-membered ring honeycomb lamellar structure having a thickness of 20 nm or less, further preferably any one or a combination of at least two of carbon six-membered ring honeycomb lamellar structures having 1-10 layers, preferably any one or a combination of at least two of single layer, double layers or 3-10 layers structures; preferably, the carbon six-membered ring honeycomb lamellar structure in the composite microscopically shows any one conformation selected from the group consisting of warping, curling and folding, and a combination of at least two selected therefrom.

The carbon nanostructure-containing composite of the present disclosure preferably comprises graphene structure and amorphous carbon; non-carbon non-oxygen non hydrogen elements are adsorbed on the surface or inside of the carbon nanostructure in a form of any one or a combination of more of simple substance, oxide, and carbide. The amorphous carbon also comprises two-dimensional graphite layers or three-dimensional graphite crystallites, on the edge of which there are a large number of irregular bonds. Besides a large number of sp2 carbons, there are many sp3 carbons. In fact, their (amorphous carbon) interior structures are crystals having the same structure as graphite, rather than real amorphous solid, besides that the layered structure formed by the hexagonal annular plane of carbon atoms is messy and irregular. There are defects in the formation of the crystal; the majority of amorphous carbon is formed by molecular debris having graphite layer structure which are roughly parallel to each other, and irregularly stacked together, referred to as chaotic layer structure. The layers or debris is connected by carbon atom bonds in the form of the tetrahedral bonding of diamond structure.

By way of example, the biomass graphene can be obtained by the method for preparing the carbon nanostructure-containing composite, which includes the following steps (labelled as method 1):

(1) catalyzing a biomass carbon source under the action of a catalyst to obtain a precursor;

(2) maintaining the temperature of the precursor at 140℃-180℃ for 1.5-2.5h under the condition of protective gas to obtain a first intermediate;

(3) heating the first intermediate to 350℃-450℃ under the condition of protective gas and maintaining the temperature for 3h-4h to obtain a second intermediate;

(4) heating the second intermediate to 1100℃-1300℃ under the condition of protective gas and maintaining the temperature for 2h-4h to obtain a third intermediate;

(5) alkali washing, acid washing and water washing the third intermediate in sequence to obtain a composite;

wherein the temperatures in steps (3) and (4) are increased at a rate of 14℃/min-18℃/min.

Preferably, the biomass carbon source is one or more of lignocellulose, cellulose and lignin.

By way of example, the biomass graphene can be obtained by the method for preparing the carbon nanostructure-containing composite, which includes the following steps (labelled as method 2):

(1) mixing a biomass carbon source and a catalyst, stirring and catalyzing, then drying to obtain a precursor;

(2) maintaining the temperature of the precursor under protective atmosphere at 280 to 350°C for 1.5 to 2.5 hours, then heating by temperature programming to 950 to 1200°C at a heating rate of 15 to 20°C/min, maintaining that temperature for 3 to 4 hours to obtain a crude product;

(3) washing the crude product to obtain a carbon nanostructure-containing composite.

In the second alternative, the biomass carbon source and the catalyst have a mass ratio of 1:(0.1-10), preferably 1:(0.5-5), further preferably 1:(1-3);

preferably, the catalyst is anyone selected from the group consisting of manganese compounds, iron-containing compound, cobalt-containing compound, nickel-containing compound, and a combination of at least two selected therefrom. Preferably, the iron-containing compound is anyone selected from the group consisting of halogen compounds of iron, iron cyanides, iron-containing salts of acid, and a combination of at least two selected therefrom. Preferably, the cobalt-containing compound is anyone selected from the group consisting of halogen compounds of cobalt, cobalt-containing salts of acid, and a combination of at least two selected therefrom. Preferably, the nickel-containing compound is anyone selected from the group consisting of nickel chlorides, nickel-containing salts of acid, and a combination of at least two selected therefrom. Preferably, the catalyst is anyone selected from the group consisting of ferric chloride, ferrous chloride, ferric nitrate, ferrous nitrate, ferric sulfate, ferrous sulfate, potassium ferricyanide, potassium ferrocyanide, potassium trioxalatoferrate, cobalt chloride, cobalt nitrate, cobalt sulfate, cobalt acetate, nickel chloride, nickel nitrate, nickel sulfate, nickel acetate, and a combination of at least two selected therefrom.

The stirring and catalyzing treatment is carried out at a temperature of 150 to 200°C for 4 hours or more, preferably 4 to 14 hours; preferably, the water content in the precursor is 10 wt% or lower; preferably, the precursor is heated to 280 to 350°C at a heating rate of 3 to 5°C/min; preferably, the protective atmosphere is any one selected from the group consisting of nitrogen, helium, argon, and a combination of at least two selected therefrom, preferably nitrogen; preferably, the crude product is subjected to acid washing and water washing successively; and the acid washing is preferably carried out by using hydrochloric acid with a concentration of 3 wt% to 6 wt%, further preferably hydrochloric acid with a concentration of 5 wt%; the water washing is preferably carried out by using deionized water and/or distilled water; preferably, the washing is carried out at a temperature of 55 to 65°C, preferably 60°C.

The biomass carbon source is cellulose and/or lignin, preferably cellulose, further preferably porous cellulose;

preferably, the porous cellulose is obtained by the following method of:

acid hydrolyzing a biomass source to obtain lignocellulose, then porous post-processing to obtain porous cellulose; optionally, the porous cellulose is used after bleaching;

Preferably, the biomass carbon source is any one selected from the group consisting of plants, agricultural and forestry wastes, and a combination of at least two selected therefrom; preferably, any one selected from agricultural and forestry wastes, and a combination of at least two selected therefrom; preferably, the agricultural and forestry wastes are any one selected from the group consisting of corn stalks, corn cobs, sorghum stalks, beet residues, bagasse, furfural residues, xylose residues, wood chips, cotton stalks, reeds, and a combination of at least two selected therefrom, preferably corn cobs.

By way of example, the biomass graphene can be obtained by the method for preparing the carbon nanostructure-containing composite, which includes the following steps (labelled as method 3):

(1') acid hydrolyzing corn cobs to obtain lignocellulose, and then porous post-processing to obtain porous cellulose, wherein the porous cellulose is bleached for standby;

(1) mixing the porous cellulose in step (1') with a catalyst in a mass ratio of 1:0.5-1.5, stirring at 150-200℃, catalyzing for 4h or more, and drying to a water content of less than 10 wt% to obtain a precursor;

(2) heating the precursor to 280-350℃ at a rate of 3-5℃/min under protective atmosphere, then heating by temperature programming to 950-1200℃ at an increasing rate of 15-20℃/min, maintaining the temperature for 3-4h to obtain a crude product;

(3) acid washing the crude product at 55-65℃ with hydrochloric acid having a concentration of 5 wt%, water washing to obtain a composite.

The carbon nanostructure-containing composite prepared by the above methods also belongs to the case of biomass containing graphene.

The biomass graphene of the present disclosure can be obtained by the following method for preparing the carbon nanostructure-containing composite:

Method 4:

The biomass source is used to obtain active carbon via current processes. Since the types and contents of microelements within different plants are greatly different, later steps such as acid washing and water washing are used to control the amount of the non-carbon non-oxygen elements. Graphene is introduced on such a basis to make the amount of the non-carbon non-oxygen element be 0.5wt%-6wt% of the composite.

Method 5

Commercially available lignose is high-temperature carbonized under inert gas, or graphitization reaction was not thoroughly carried out. Then graphene is added. A combination of any three or more selected from nano-P, Si, Ca, Al, Na, Fe, Ni, Mn, K, Mg, Cr, S or Co is introduced later, and the content thereof is controlled to be 0.5wt%-6wt%.

Method 6

Some organic wastes such as phenolic resin cystosepiment are carbonized. Then graphene is added. A combination of any three or more selected from nano-P, Si, Ca, Al, Na, Fe, Ni, Mn, K, Mg, Cr, S or Co is introduced later, and the content thereof is controlled to be 0.5wt%-6wt%.

Method 7

Active carbon and graphene are added to nano-graphite. A combination of any three or more selected from nano-P, Si, Ca, Al, Na, Fe, Ni, Mn, K, Mg, Cr, S or Co is introduced later, and the content thereof is controlled to be 0.5wt%-6wt%.

The preparation of the biomass graphene of the present disclosure is not limited to the above preparation methods. The biomass graphenes obtained by the methods 1-3 are superior to those obtained by the methods 4-7 in terms of the far infrared and bacteria resistance properties. However, all the biomass graphenes can be dispersed uniformly in the modified fiber without activation or modification treatment when the down-stream products are produced, which can play a certain effect, especially for methods 1-3.

Preferably, the content of graphene in the modified hollow cotton is 0.2-10 wt%, preferably 0.3-8 wt%, further preferably 0.5-5 wt%.

By way of example, the content of graphene in the modified hollow cotton according to the present disclosure is 0.3 wt%, 0.6 wt%, 0.9 wt%, 1.1 wt%, 1.4 wt%, 1.6 wt%, 1.8 wt%, 2.1 wt%, 2.4 wt%, 2.5 wt%, 2.8 wt%, 3.0 wt%, 3.4 wt%, 3.6 wt%, 3.9 wt%, 4.2 wt%, 4.5 wt%, 4.9 wt%, 5.2 wt%, 5.8 wt%, 6.3 wt%, 6.5 wt%, 6.6 wt%, 6.9 wt%, 7.3 wt%, 7.5 wt%, 7.9 wt%, 8.2 wt%, 8.8 wt%, 9.3 wt%, and 9.9 wt%, etc.

Preferably, the doping amount of graphene in the modified polyamide fiber is 0.2-10 wt%, preferably 0.3-8 wt%, further preferably 0.5-5 wt%.

By way of example, the doping amount of graphene in the modified polyamide fiber according to the present disclosure is 0.3 wt%, 0.6 wt%, 0.9 wt%, 1.1 wt%, 1.4 wt%, 1.6 wt%, 1.8 wt%, 2.1 wt%, 2.4 wt%, 2.5 wt%, 2.8 wt%, 3.0 wt%, 3.4 wt%, 3.6 wt%, 3.9 wt%, 4.2 wt%, 4.5 wt%, 4.9 wt%, 5.2 wt%, 5.8 wt%, 6.3 wt%, 6.5 wt%, 6.6 wt%, 6.9 wt%, 7.3 wt%, 7.5 wt%, 7.9 wt%, 8.2 wt%, 8.8 wt%, 9.3 wt%, and 9.9 wt%, etc.

Preferably, the far infrared detection normal emissivity of the modified hollow cotton according to the present disclosure is greater than 0.85, for example 0.87, 0.89, 0.91, 0.92, and 0.93, etc., preferably greater than 0.88.

The thermal insulation effect of the modified hollow cotton provided by the present disclosure is 1 kg of the modified hollow cotton of the present disclosure has the same thermal insulation effect as that of 2.5-3 kg of ordinary hollow cotton, and the air permeability is good while ensuring the thermal insulation effect.

Preferably, the far infrared detection normal emissivity of the modified polyamide fiber according to the present disclosure is greater than 0.85, for example 0.87, 0.89, 0.91, 0.92, and 0.93, etc., preferably greater than 0.88.

The modified polyamide fiber provided by the present disclosure has far-infrared function, and the socks or clothes made therefrom have far-infrared emission, which can protect human joints from catching cold; in addition, the modified polyamide fiber with addition of graphene has bacteria resistance and inhibition effects, and the fabrics, etc., made therefrom will not produce odors during long-term use.

The second object of the present disclosure is to provide another method for preparing the modified hollow cotton as described in the first object, which includes the following steps:

(A'-1) mixing graphene with blank polyester chips, screw extruding, and drying to obtain graphene-containing polyester masterbatches;

(A'-2) uniformly mixing the graphene-containing polyester masterbatches with a portion of blank polyester chips, and then mixing with the remaining blank polyester chips b;

(A'-3) melt spinning the resulting materials, and then opening to obtain the modified hollow cotton;

The present disclosure adopts a physical method to disperse solid graphene into the polyester substrate, thereby obtaining a modified hollow cotton containing uniformly dispersed graphene. Specifically, according to the present disclosure, the hollow cotton containing uniformly dispersed graphene is obtained by firstly mixing the blank polyester chips with solid graphene, screw extruding the mixture to obtain graphene composite polyester masterbatches, in which polyester masterbatches serve as carrier of graphene for primary dispersion of graphene; then, physically mixing the graphene-loaded polyester masterbatches with the blank polyester chips in two steps according to the formulation amount to obtain the materials to be spun, in which the graphene is uniformly dispersed; finally, spinning according to the conventional preparation process of hollow cotton to obtain the hollow cotton containing uniformly dispersed graphene. The method of the present disclosure solves the technical problem of uneven dispersion of graphene in the related technologies, and obtains a modified hollow cotton showing excellent thermal insulation property, air permeability, low-temperature far-infrared and bacteria resistance properties.

In the present disclosure, primary dispersion is achieved by firstly dispersing the graphene particles which are easy to agglomerate in the blank polyester chips, and then physically mixing the obtained masterbatches with the blank polyester chips in two steps to achieve uniform dispersion of the graphene, thereby obtaining the uniformly dispersed materials to be spun.

preferably, the blank polyester chips of step (A'-1) and step (A'-2) are each independently PET and/or PBT.

Preferably, the blank polyester chips of step (A'-1) are PET.

The selection of the blank polyester chips according to step (A'-1) and step (A'-2) of the present disclosure is not specifically limited, and they can be selected by a person skilled in the art according to actual situations. However, the melting point of PET is about 220°C, and the melting point of PBT is about 270°C. From the view of energy saving of the process temperature, the blank polyester chips of the present disclosure are preferably PET.

Preferably, the graphene content in the graphene-containing polyester masterbatches is 1-20wt%, for example 2 wt%, 4 wt%, 6 wt%, 8 wt%, 12 wt%, 15 wt%, 17 wt%, 19wt%, etc., preferably 5-15 wt%, further preferably 6-10 wt%.

Preferably, the melting temperature of the screw extrusion of step (A'-1) is 230-270°C, for example 235°C, 240°C, 244°C, 249°C, 253°C, 258°C, 262°C, 267°C, etc., preferably 240-260°C.

Preferably, the moisture content of the graphene-containing polyester masterbatches is 600 ppm or less, for example 50 ppm, 80 ppm, 130 ppm, 180 ppm, 230 ppm, 280 ppm, 350 ppm, 390 ppm, 420 ppm, 450 ppm, 480 ppm, etc., preferably 300 ppm or less.

Preferably, the mass ratio of the graphene-containing polyester masterbatches to the blank polyester chips in step (A'-2) is 1:(5-30), for example 1:6, 1:7, 1:9, 1:13, 1:16, 1:22, 1:26, 1:29, etc., preferably 1:(15-20).

Preferably, in step (A'-2), the ratio of the part of the blank polyester chips to the integral blank polyester chips added in step (b) is 1:(2-10), for example 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9, etc., preferably 1:(4-8).

The integral blank polyester chip b refers to the sum of the masses of the part of the blank polyester chips b and the remaining blank polyester chips b.

Preferably, the intrinsic viscosity of the raw materials for melt spinning in step (A'-3) is 0.60 dL/g or more, for example 0.62 dL/g, 0.66 dL/g, 0.69 dL/g, 0.72 dL/g, 0.75 dL/g, 0.78 dL/g, 0.80d L/g, and 0.85 dL/g, etc., preferably 0.65 dL/g or more.

The addition of graphene of the present disclosure will reduce the viscosity of the chips, however the spinning step cannot be performed if the viscosity is too low.

Preferably, step (A'-1') is performed before step (A'-1): smashing the blank polyester chips into blank polyester chip particles for mixing with the graphene of step (A'-1);

preferably, the particle size of the blank polyester chip particles is 3 mm or less, for example 0.1 mm, 0.5 mm, 0.9 mm, 1.3 mm, 1.8 mm, 2.2 mm, 2.5 mm, 2.8 mm, etc.

In step (a'), blank polyester chips are chopped to increase the rough surface, which increases the specific surface area and frictional force of the graphene attached thereto, and further improving the dispersibility of the graphene.

Further preferably, step (A'-2') is set between step (A'-2) and step (A'-3): screw extruding the materials uniformly mixed in step (A'-2) again;

preferably, the melting temperature of the screw extrusion of the modified hollow cotton is 230-270°C, for example 235°C, 240°C, 244°C, 249°C, 253°C, 258°C, 262°C, 267°C, etc., preferably 240-260°C.

After the conventional polyester is subjected to the screw extrusion twice, the cleavage of the polyester polymer molecules will be caused, which reduces the length of its molecular chain and the strength of the polyester, eventually resulting in insufficient wiredrawing length during the process of preparing the hollow cotton; by means of adding graphene particles to the polyester substrate in the present disclosure, the melting temperature of the screw extrusion can be improved, even if the screw extrusion is performed twice, the length of the molecular chain of the obtained polyester fiber has less change, enabling the preparation of the hollow cotton fiber.

As an optional technical solution, a method for preparing the hollow cotton according to the present disclosure includes the following steps:

(A'-1') smashing PET blank chips to obtain PET blank chip particles;

(A'-1) mixing graphene with PET blank chip particles, then screw extruding at a melting temperature of 230-270°C, drying the extruded product to a moisture content of 600 ppm or less to obtain graphene-containing PET polyester masterbatches;

(A'-2) mixing the graphene-containing PET polyester masterbatches with PET polyester chips to obtain materials with intrinsic viscosity of 0.60 dL/g or more;

(A'-3) melt spinning the resulting materials, and then opening to obtain the hollow cotton.

The third object of the present disclosure is to provide another method for preparing a modified polyamide fiber as described in the first object, which includes the following steps:

(B'-1) mixing graphene with blank polyamide chips, screw extruding, and drying to obtain graphene-containing polyamide masterbatches;

(B'-2) uniformly mixing the graphene-containing polyamide masterbatches with a portion of blank polyamide chips, and then mixing with the remaining blank polyamide chips b;

(B'-3) melt spinning the resulting materials to obtain the modified polyamide fiber.

The present disclosure adopts a physical method to disperse solid graphene into the polyamide substrate, thereby obtaining a modified polyamide fiber containing uniformly dispersed graphene. Specifically, according to the present disclosure, the modified polyamide fiber containing uniformly dispersed graphene is obtained by firstly mixing the blank fiber chips with solid graphene, screw extruding the mixture to obtain graphene composite fiber masterbatches, in which fiber masterbatches serve as carrier of graphene for primary dispersion of graphene; then, physically mixing the graphene-loaded fiber masterbatches with the blank fiber chips in two steps according to the formulation amount to obtain the materials to be spun, in which the graphene is uniformly dispersed; finally, spinning according to the conventional preparation process of polyamide spinning to obtain the modified polyamide fiber containing uniformly dispersed graphene. The method of the present disclosure solves the technical problem of uneven dispersion of graphene in the related technologies, and obtains a modified polyamide fiber showing excellent low-temperature far-infrared and bacteria resistance properties.

In the present disclosure, primary dispersion is achieved by firstly dispersing the graphene particles which are easy to agglomerate in the blank polyamide chips, and then physically mixing the obtained masterbatches with the blank polyamide chips in two steps to achieve uniform dispersion of the graphene, thereby obtaining the uniformly dispersed materials to be spun.

Preferably, the blank polyamide chips of step (B'-1) and step (B'-2) are each independently any one of PA-6, PA-66, PA-610, PA-1010, and MCPA.

The selection of the blank polyamide chips according to step (B'-1) and step (B'-2) of the present disclosure is not specifically limited, and they can be selected by a person skilled in the art according to actual situations.

Preferably, the graphene content in the graphene-containing polyamide masterbatches is 3-10 wt%, for example 4 wt%, 6 wt%, 8 wt%, 9 wt%, etc., preferably 5-8 wt%.

Preferably, the melting temperature of the screw extrusion of step (B'-1) is 210-240°C, for example 215°C, 217°C, 221°C, 225°C, 228°C, 231°C, 234°C, 238°C, etc., preferably 240-260°C.

Preferably, the moisture content of the graphene-containing polyamide masterbatches is 600 ppm or less, for example 50 ppm, 80 ppm, 130 ppm, 180 ppm, 230 ppm, 280 ppm, 350 ppm, 390 ppm, 420 ppm, 450 ppm, 480 ppm, etc., preferably 300 ppm or less.

Preferably, the mass ratio of the graphene-containing polyamide masterbatches to the blank polyamide chips in step (B'-2) is 1:(5-30), for example 1:6, 1:7, 1:9, 1:13, 1:16, 1:22, 1:26, 1:29, etc., preferably 1:(15-20).

Preferably, in step (B'-2), the ratio of the part of the blank polyamide chips to the integral blank polyamide chips added in step (B'-2) is 1:(2-10), for example 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9, etc., preferably 1:(4-8).

The integral blank polyamide chip refers to the sum of the masses of the part of the blank polyamide chips and the remaining blank polyamide chips.

Preferably, the intrinsic viscosity of the raw materials for melt spinning in step (B'-3) is 3 dL/g or less, preferably 2.7 dL/g or less.

The addition of graphene of the present disclosure will increase the viscosity of the chips, however the spinning step cannot be performed if the viscosity is too high.

As a preferred technical solution, step (B'-1') is performed before step (B'-1): smashing the blank polyamide chips into blank polyamide chip particles for mixing with the graphene of step (B'-1);

preferably, the particle size of the blank polyamide chip particles is 3 mm or less, for example 0.1 mm, 0.5 mm, 0.9 mm, 1.3 mm, 1.8 mm, 2.2 mm, 2.5 mm, 2.8 mm, etc.

In step (B'-1'), blank polyamide chips are chopped to increase the rough surface, which increases the specific surface area and frictional force of the graphene attached thereto, and further improving the dispersibility of the graphene.

Further preferably, step (B'-2') is set between step (B'-2) and step (B'-3): screw extruding the materials uniformly mixed in step (B'-2) again;

preferably, the melting temperature of the screw extrusion in the preparation method of the modified polyamide fiber is 210-240°C, for example 215°C, 217°C, 221°C, 225°C, 228°C, 231°C, 234°C, 238°C, etc., preferably 240-260°C.

After the conventional polyamide is subjected to the screw extrusion twice, the cleavage of the polyamide polymer molecules will be caused, which reduces the length of its molecular chain and the strength of the polyamide, eventually resulting in insufficient wiredrawing length during the process of preparing the modified polyamide fiber; by means of adding graphene particles to the polyamide substrate in the present disclosure, the melting temperature of the screw extrusion can be improved, even if the screw extrusion is performed twice, the length of the molecular chain of the obtained polyamide fiber has less change, enabling the preparation of the modified polyamide fiber.

The third object of the present disclosure is to provide one method for preparing a modified hollow cotton as described in the first object, which includes the following steps:

(A-1) smashing blank polyester chip to obtain blank polyester chip particles;

(A-2) mixing graphene with blank polyester chip particles, screw extruding, and drying to obtain graphene-containing polyester masterbatches;

(A-3) uniformly mixing the graphene-containing polyester masterbatches with the blank polyester chips;

(A-4) melt spinning the resulting materials, and then opening to obtain the modified hollow cotton.

The present disclosure adopts a physical method to disperse solid graphene into the polyester substrate, thereby obtaining a modified hollow cotton containing uniformly dispersed graphene. Specifically, according to the present disclosure, the hollow cotton containing uniformly dispersed graphene is obtained by firstly chopping the blank polyester chips to increase the rough surface, so as to increase the specific surface area and frictional force of the graphene attached thereto, which will improve the dispersibility of the graphene; then dispersing the solid graphene in the blank polyester chip particles, screw extruding the mixture to obtain graphene composite polyester masterbatches, in which polyester masterbatches serve as carrier of graphene for primary dispersion of graphene; then, physically mixing the graphene-loaded polyester masterbatches with the blank polyester chips according to the formulation amount to obtain the materials to be spun, in which the graphene is uniformly dispersed; finally, melt spinning according to the conventional preparation process of hollow cotton to obtain the modified hollow cotton uniformly doped with graphene. The method of the present disclosure solves the technical problem of uneven dispersion of graphene in the related technologies, and obtains a modified hollow cotton showing excellent thermal insulation property, air permeability, low-temperature far-infrared and bacteria resistance properties.

In the present disclosure, primary dispersion is achieved by dispersing the graphene particles which are easy to agglomerate in the blank polyester chip particles, and then mixing the obtained masterbatches with the blank polyester chips again to obtain the uniformly dispersed materials to be spun.

The blank polyester chips of the present disclosure refers to the polyester chips without adding functional graphene particles.

Uniform distribution refers to: the probabilities of the measured values appearing in a certain range are the same. For this application, the uniform dispersion means that the content of graphene in the modified hollow cotton is less different for any cubic centimeter ranges.

Preferably, the particle size of the blank polyester chip particles is 3 mm or less, for example 0.1 mm, 0.5 mm, 0.9 mm, 1.3 mm, 1.8 mm, 2.2 mm, 2.5 mm, 2.8 mm, etc.

Preferably, the blank polyester chips of step (A-1) and step (A-3) are each independently PET (polyethylene terephthalate) and/or PBT (polybutylene terephthalate).

Preferably, the blank polyester chips of step (A-1) are PET.

The selection of the blank polyester chips according to step (A-1) and step (A-3) of the present disclosure is not specifically limited, and they can be selected by a person skilled in the art according to actual situations. However, the melting point of PET is about 220°C, and the melting point of PBT is about 270°C. From the view of energy saving of the process temperature, the first blank polyester chips of the present disclosure are preferably PET, and the second blank polyester chips are PET.

Preferably, the graphene content in the graphene-containing polyester masterbatches is 1-20 wt%, for example 2 wt%, 4 wt%, 6 wt%, 8 wt%, 12 wt%, 15 wt%, 17 wt%, 19 wt%, etc., preferably 5-15 wt%, most preferably 6-10 wt%.

Preferably, the melting temperature of the screw extrusion of step (A-2) is 230-270°C, for example 235°C, 240°C, 244°C, 249°C, 253°C, 258°C, 262°C, 267°C, etc., preferably 240-260°C.

Preferably, the moisture content of the graphene-containing polyester masterbatches is 600 ppm or less, for example 50 ppm, 80 ppm, 130 ppm, 180 ppm, 230 ppm, 280 ppm, 350 ppm, 390 ppm, 420 ppm, 450 ppm, 480 ppm, etc., preferably 300 ppm or less.

Preferably, the mass ratio of the graphene-containing polyester masterbatches to the blank polyester chips in step (A-3) is 1:(5-30), for example 1:6, 1:7, 1:9, 1:13, 1:16, 1:22, 1:26, 1:29, etc., preferably 1:(15-20).

Preferably, the intrinsic viscosity of the raw materials for melt spinning in step (A-4) is 0.60 dL/g or more, for example 0.62 dL/g, 0.66 dL/g, 0.69 dL/g, 0.72 dL/g, 0.75 dL/g, 0.78 dL/g, 0.80d L/g, and 0.85 dL/g, etc., preferably 0.65 dL/g or more.

The addition of graphene of the present disclosure will reduce the viscosity of the chips, however the spinning step cannot be performed if the viscosity is too low.

As a preferred technical solution, mixing the graphene-containing polyester masterbatches with the blank polyester chips in step (A-3) of the present disclosure includes the following steps:

(A-3a) uniformly mixing the graphene-containing polyester masterbatches with a part of the blank polyester chips;

(A-3b) continuously adding the remaining blank polyester chips to the mixture of step (A-3a) to mix uniformly.

The graphene-containing polyester masterbatches is diluted and dispersed in two steps with polyester chips, so that the concentration of the graphene particles reaches a predetermined requirement, and the graphene can be dispersed more uniformly, the modified hollow cotton obtained can exhibit more excellent thermal insulation, low-temperature far-infrared and bacteria resistance properties.

Preferably, in step (A-3a), the mass ratio of the part of the blank polyester chips to the integral blank polyester chip added in step (A-3a) is 1:(2-10), for example 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9, etc., preferably 1:(4-8).

The integral blank polyester chip added in step (A-3a) refers to the sum of the masses of the part of the blank polyester chips and the remaining blank polyester chips.

Further preferably, step (A-3') is set between step (A-3) and step (A-4): screw extruding the materials uniformly mixed in step (A-3) again;

Preferably, the melting temperature of the screw extrusion is 230-270°C, for example 235°C, 240°C, 244°C, 249°C, 253°C, 258°C, 262°C, 267°C, etc., preferably 240-260°C.

After the conventional polyester is subjected to the screw extrusion twice, the cleavage of the polyester polymer molecules will be caused, which reduces the length of its molecular chain and the strength of the polyester, eventually resulting in insufficient wiredrawing length during the process of preparing the hollow cotton; by means of adding graphene particles to the polyester substrate in the present disclosure, the melting temperature of the screw extrusion can be improved, even if the screw extrusion is performed twice, the length of the molecular chain of the obtained polyester fiber has less change, enabling the preparation of the hollow cotton fiber.

As an optional technical solution, a method for preparing the hollow cotton according to the present disclosure includes the following steps:

(A-1) smashing PET blank chips to obtain PET blank chip particles;

(A-2) mixing graphene with PET blank chip particles, then screw extruding at a melting temperature of 230-270°C, drying the extruded product to a moisture content of 600 ppm or less to obtain graphene-containing PET polyester masterbatches;

(A-3) mixing the graphene-containing PET polyester masterbatches with PET polyester chips to obtain materials with intrinsic viscosity of 0.60 dL/g or more;

(A-4) melt spinning the resulting materials, and then opening to obtain the modified hollow cotton.

The second object of the present disclosure is to provide a method for preparing a modified polyamide fiber as described in the first object, which includes the following steps:

(B-1) smashing blank polyamide chips to obtain blank polyamide chip particles;

(B-2) mixing graphene with blank polyamide chip particles, screw extruding, and drying to obtain graphene-containing polyamide masterbatches;

(B-3) uniformly mixing the graphene-containing polyamide masterbatches with the blank polyamide chips;

(B-4) melt spinning the resulting materials to obtain the modified polyamide fiber.

The present disclosure adopts a physical method to disperse solid graphene into the polyamide substrate, thereby obtaining a modified polyamide fiber containing uniformly dispersed graphene. Specifically, according to the present disclosure, the hollow cotton containing uniformly dispersed graphene is obtained by firstly chopping the blank polyamide chips to increase the rough surface, so as to increase the specific surface area and frictional force of the graphene attached thereto, which will improve the dispersibility of the graphene; then dispersing the solid graphene in the blank polyamide chip particles, screw extruding the mixture to obtain graphene composite polyamide masterbatches, in which polyamide masterbatches serve as carrier of graphene for primary dispersion of graphene; then, physically mixing the graphene-loaded polyamide masterbatches with the blank polyamide chips according to the formulation amount to obtain the materials to be spun, in which the graphene is uniformly dispersed; finally, melt spinning according to the conventional spinning preparation process of polyamide fiber to obtain the modified polyamide fiber uniformly doped with graphene. The method of the present disclosure solves the technical problem of uneven dispersion of graphene in the related technologies, and obtains a modified polyamide fiber showing excellent thermal insulation property, air permeability, low-temperature far-infrared and bacteria resistance properties.

In the present disclosure, primary dispersion is achieved by dispersing the graphene particles which are easy to agglomerate in the blank polyamide chip particles, and then mixing the obtained masterbatches with the blank polyamide chips again to obtain the uniformly dispersed materials to be spun.

The blank polyamide chips of the present disclosure refers to the polyamide chips without adding functional graphene particles.

Uniform distribution refers to: the probabilities of the measured values appearing in a certain range are the same. For this application, the uniform dispersion means that the content of graphene in the modified polyamide fiber is less different for any cubic centimeter ranges.

preferably, the particle size of the blank polyamide chip particles is 3 mm or less, for example 0.1 mm, 0.5 mm, 0.9 mm, 1.3 mm, 1.8 mm, 2.2 mm, 2.5 mm, 2.8 mm, etc.

Preferably, the blank polyamide chips of step (1) and step (3) are each independently any one of PA-6, PA-66, PA-610, PA-1010, and MCPA.

The selection of the blank polyamide chips according to step (B-1) and step (B-3) of the present disclosure is not specifically limited, and they can be selected by a person skilled in the art according to the actual situations.

Preferably, the graphene content in the graphene-containing polyamide masterbatches is 3-10 wt%, for example 4 wt%, 6 wt%, 8 wt%, 9 wt%, preferably 5-8 wt%.

Preferably, the melting temperature of the screw extrusion of step (B-2) is 210-240°C, for example 215°C, 217°C, 221°C, 225°C, 228°C, 233°C, 236°C, 238°C, etc., preferably 220-230°C.

The addition of graphene will affect the melting temperature of the extruded plastics of polyamide. Too high melting temperature will cause the polyamide molecular chain to break, affecting the strength of polyamide fiber, instead too low melting temperature will not achieve the base of polyamide fiber.

Preferably, the moisture content of the graphene-containing polyamide masterbatches is 600 ppm or less, for example 50 ppm, 80 ppm, 130 ppm, 180 ppm, 230 ppm, 280 ppm, 350 ppm, 390 ppm, 420 ppm, 450 ppm, 480 ppm, etc., preferably 300 ppm or less.

Preferably, the mass ratio of the graphene-containing polyamide masterbatches to the blank polyamide chips in step (B-3) is 1:(5-30), for example 1:6, 1:7, 1:9, 1:13, 1:16, 1:22, 1:26, 1:29, etc., preferably 1:(15-20).

Preferably, the intrinsic viscosity of the raw materials for melt spinning in step (B-4) is 3 dL/g or less, preferably 2.7 dL/g or less.

The addition of graphene of the present disclosure will increase the viscosity of the polyamide chips, however the spinning step will be affected if the viscosity is too high.

As a preferred technical solution, mixing the graphene-containing polyamide masterbatches with the blank polyamide chips in step (B-3) of the present disclosure includes the following steps:

(B-3a) uniformly mixing the graphene-containing polyamide masterbatches with a part of the blank polyamide chips;

(B-3b) continuously adding the remaining blank polyamide chips to the mixture of step (B-3a) to mix uniformly.

The graphene-containing polyamide masterbatches is diluted and dispersed in two steps with polyamide chips, so that the concentration of the graphene particles reaches a predetermined requirement, and the graphene can be dispersed more uniformly, no harsh process condition for melt spinning is needed, and the modified polyamide fiber obtained can maintain good strength while exhibiting excellent low-temperature far-infrared and bacteria resistance properties.

Preferably, in step (B-3a), the mass ratio of the part of the blank polyamide chips to the integral blank polyamide chip added in step (B-3a) is 1:(2-10), for example 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9, etc., preferably 1:(4-8).

The integral blank polyamide chip added in step (B-3a) refers to the sum of the masses of the part of the blank polyamide chips and the remaining blank polyamide chips.

Further preferably, step (B-3') is set between step (B-3) and step (B-4): screw extruding the materials uniformly mixed in step (B-3) again;

Preferably, the melting temperature of the screw extrusion is 210-240°C, for example 215°C, 217°C, 219°C, 224°C, 227°C, 228°C, etc., preferably 240-260°C.

After the conventional polyamide is subjected to the screw extrusion twice, the cleavage of the polyamide polymer molecules will be caused, which reduces the length of its molecular chain and the strength of the polyamide, eventually resulting in insufficient wiredrawing length during the process of preparing the modified polyamide fiber; by means of adding graphene particles to the polyamide substrate in the present disclosure, the melting temperature of the screw extrusion can be improved, even if the screw extrusion is performed twice, the length of the molecular chain of the obtained polyamide fiber has less change, enabling the preparation of the modified polyamide fiber.

As an optional technical solution, a method for preparing the modified polyamide fiber according to the present disclosure includes the following steps:

(B-1) smashing blank polyamide chips to obtain blank polyamide chip particles;

(B-2) mixing graphene with blank polyamide chip particles, then screw extruding at a melting temperature of 210-240°C, drying the extruded product to a moisture content of 600 ppm or less to obtain graphene-containing polyamide masterbatches;

(B-3) mixing the graphene-containing polyamide masterbatches with blank polyamide chips to obtain materials with intrinsic viscosity of 3 dL/g or less;

(B-4) melt spinning the resulting materials, then opening to obtain the modified polyamide fiber.

In the method for producing the modified fiber according to the present disclosure, the spinning (step (A-4), step (V-4), step (A'-3) or step (B'-3)) of step (A'-3), step (B'-3), step (A-4), and step (B-4) is well known in the art.

Melt spinning method is to obtain hollow fiber through hollow spinneret plate, which is economical and reasonable, the relevant technologies are mature, and process conditions can be controlled.

Melt spinning is carried out by inserting a microporous tube into a hollow spinneret plate and filling the cavity of the fiber with nitrogen or air to obtain an inflated hollow fiber with high hollowness, avoiding the reduction of the hollowness due to flattening of the fiber by mechanical actions during the production process. In addition, the thermal conductivity of the fiber is worse than that of air, which greatly improves the warmth retention property. The control of the gas flow is a well-known method in the art. Those skilled in the art can also change the shape of the spinneret orifice to produce hollow fibers with various profiled cross-sections such as triangle and quincunx, etc., to increase the specific surface area of the fibers, or to obtain porous hollow fibers with 3 to 7 holes through special spinneret plates, but the hollowness of which may not be high, being only within 30%. Hollow fiber or three-dimensional crimped hollow fiber can also be obtained by those skilled in the art through direct melt spinning with designing the shape of the spinneret plate and properly adjusting the spinning process (asymmetric cooling with circular blowing and post-spinning stretch controlling technology).

As is well known to those skilled in the art, a desired hollowness can be achieved by adjusting the process conditions of melt spinning. Typical but not limiting process conditions can be:

(1) design of the spinneret plate for melt spinning of the hollow fiber

The design of the spinneret plate includes both its shape and structural dimensions. The former is used for hollow fibers with profiled cross-sections, and the design of which is related to the production requirements, and the commonly used hole shapes include polygonal, c-shaped, circular arc, multi-point shapes, etc. The design of the structural dimensions of the spinneret plate can include feature size data such as the slit length of the spinneret orifices, the distance between the tips of two slits, the equivalent diameters, the cross-sectional area, the aspect ratio, and the like;

A typical, but non limiting example of preparation of warmth retention three-dimensional crimped hollow fibers by melt-spinning is the use of a circular arc slit spinneret plate, by which fibers with finer outer diameter and suitable hollowness can be easily spun. At present, the circular arc slit spinneret plates with good effect mainly include C-shaped and triangle-shaped spinneret plates and porous hollow fiber spinneret plates with circular arc combinations, etc, which are used to spin hollow fibers of four-hole, seven-hole and even dozen-hole. After the melt is extruded out of the circular arc slit of the spinneret plate, the circular arc-shaped melt expands and and the ends of which binds to form a hollow cavity, which is thinned and solidified to form a hollow fiber.

As is well known in the art, the size of the gap in the circular arc slit of the spinneret plate may affect the formation of the hollow cavity: when the gap is too large, the hollow of the fibers cannot be closed and only the opening fibers can be spun; but when the gap is too small, the melt will quickly expand and bond after extrude from the spinneret orifice, so that the hollow cavity cannot be formed. Moreover, from the viewpoint of mechanical strength, the smaller the gap of the spinneret plate is, the lower the strength is, and the spinneret plate is easily damaged. Therefore, for materials with different properties, there are different suitable sizes of gaps in the spinneret plates. Typical but non limiting example is the expanding ratio of the die orifice for the extrusion of the melt materials can guide the design of the size of the gaps in the spinneret plates, and the width ratio at the center of the gaps is slightly less than the expansion ratio of the die orifice for the melt materials.

For the spinneret hole, if the slit width is large, the extrusion volume of a single hole is large, the cross-sectional area of the spun fiber is large, and the hollowness of the fiber is small; the slit width is small, the extrusion volume of a single hole is small, and the hollowness of the spun fiber is large. However, if the slit is too small, the wall of the spun fiber is too thin, the hollow regularity is low, and the hollow is easy to deform. For the C-shaped spinneret plate, the width at the center of the gap is equal to 1.0-fold of the slit width; for the triangle-shaped spinneret plate, the width at the center of the gap is equal to 0.8-fold of the slit width. A person skilled in the art has ability to set the specific sizes of the gap and slit of the spinneret plate according to the product requirements and the different properties of the spinning materials.

In addition to the C-shaped and triangle-shaped spinneret plates for melt spinning of the hollow fiber films, there may also exist double circular and double circular sleeved spinneret plates. The hollow fibers spun by the latter two spinneret plates have uniform inner and outer diameters and good concentricity. Due to the support of the gap materials in the c-shaped and the triangle-shaped spinneret plates, they can be easily used to shape a plurality of single holes simultaneously on one spinneret plate for spinning filament beam with large production. However, since the double circular and double circular sleeved spinneret plates are composed of a plurality of components, it is difficult to make multi-hole spinneret plates, and most of them are used only for spinning single hollow fiber films.

(2) Asymmetric cooling with circular blowing

As well known to those skilled in the art, factors affecting the hollowness of the melt-spun hollow fibers include factors such as spinning temperature, and cooling and shaping conditions, etc. in addition to size of spinneret plate; if the spinning temperature is high, the melt viscosity is small, and the expansion phenomenon of melt after exiting the spinneret hole is greatly reduced, the resistance to melt deformation decreases, and the surface tension also decreases, which causing the melt trickle to produce surface shrink, so that the cavity portion becomes smaller, and the spun hollowness decreases.

Cooling and shaping conditions include conditions such as wind speed, wind temperature, and blowing distance, etc., which have a great influence on the physical parameters such as rheological properties of the melt trickle in the spinning path, for example the elongational flow viscosity and tensile stress, etc., and directly determine the hollowness.

Typically, as the wind speed increases, the cooling conditions intensify, the solidifying rate of the melt trickle increases, so that the cavities in the hollow fibers formed on the spinning path are less likely to shrink and quickly solidify, which is favorable to the formation of cavities of hollow fibers, so that the fiber has a high hollowness, but if the wind speed is too high, it will cause the silk sliver to shake and produce turbulence, thereby decreasing the temperature of the plate surface of the spinneret plate, so that the silk yarn cannot be smoothly drawn, the hardhead filament and doubling will be easily produced, causing broken end. As the wind temperature decreases, the cooling and shaping conditions are strengthened, increasing the solidification rate of the melt trickle, and the hollowness of the spun fiber is high. However, if the air temperature is too low, the plate surface of the spinneret plate is easy to be blown cold, so that the spinning becomes difficult. For double circular sleeved spinneret plates, the size of the gas flow passing through the sleeve may also affect the hollowness of the fibers. A person skilled in the art has ability to prepare a hollow fiber film with suitable hollowness by selecting the ratio of the gas supply amount to the pumping amount of the spinning slurry.

A person skilled in the art can reduce the formation of three-dimensional crimps and prevent deterioration of the post-spinning tensile properties of the hollow fibers obtained by direct melt spinning through controlling the asymmetric cooling with circular blowing. The asymmetric cooling with circular blowing process includes four aspects of blowing speed, temperature and humidity, as well as uniformity. Increasing the wind speed can enhance the asymmetrical structure of the fiber's cross-section to obtain as-spun fibers with potentially better crimp. However, if the wind speed is too high, causing the silk sliver to oscillate, so that the silk yarn cannot be smoothly drawn, the pre-orientation degree of the precursor fibers may be large, and the tensile properties may deteriorate, etc. Therefore, a person skilled in the art can select an appropriate wind speed to balance the potential crimp and the tensile properties of the precursor fibers; although reducing the circular blowing wind temperature makes the cooling conditions intensify, the pre-orientation of the precursor fibers increases at the same time, and the tensile properties decrease, thus it is also necessary for a person skilled in the art to select a suitable wind temperature; and the circular blowing wind can also have a certain humidity to reduce the electrostatic phenomenon and turbulence of silk sliver in the spinning process, and control the cooling conditions; at the same time, the uniformity of the circular blowing wind is increased to ensure stable spinning and post-spinning tensile properties.

(3) Post-spinning stretch

The purpose of stretching the three-dimensional crimped hollow fibers is not to improve the mechanical properties of the fibers, but to embody the stress difference and potential crimp inside the as-spun fibers. It is necessary to not only pull apart the stress difference on the cross-section of each single fiber during the stretching as much as possible, but also keep such differences between single fibers at the same level, therefore one-stretch process is generally used for hollow fibers.

Stretching method, stretching temperature and stretching ratio are technical parameters in post-spinning stretch, and those skilled in the art can select according to their own professional knowledges. Typical, but without limitation, there are steam stretching and water bath stretching according to the stretching medium: the water bath stretching takes the heated oil and water as medium, and the fibers produce a secondary orientation during stretching, resulting in a decrease in the intrinsic structural difference of the fibers, and reduction in the crimp and fluffy properties; whereas the steam stretching uses saturated steam as the medium, therefore it is adiabatic stretching, and the orientation is completed at one time. Comparatively speaking, the crystal structure of the fibers after steam stretching is more pronounced and stable. Both the stretching ratio and the temperature must be chosen by taking into consideration of both the tensile properties of the as-spun fibers and the release of the crimp.

(4) Control technology of hollowness

The hollow control of the hollowness runs through the entire melt spinning process. There is a control of the hollowness from the size of the spinneret orifice to the post-spinning stretch process. The typical but non-limiting slit width of the spinneret orifice and the distance between the tips of the two slits are suitable preconditions for the hollowness of the spun circular hollow fibers; and the spinning temperature and the cooling and shaping conditions are the main process factors for controlling the hollowness. Low spinning temperature, large melt viscosity, and large melt deformation resistance and the surface tension are beneficial to the formation of hollow, but too low of these will cause hard filaments, etc.; and as the stretching ratio increases, the fiber walls become thinner, resulting in the increased hollowness. In addition, those skilled in the art can also investigate the process conditions such as moisture content of chips (generally dehumidified by the compressed air through a molecular sieve drying device), spinning temperature and speed, relaxation heat setting process, and oiling agent formulation and oiling mode of the silicon-containing products, etc. needed to be controlled in the conventional spinning.

As the melt spinning process is well known in the art, those skilled in the art can consult the background technology according to their own professional knowledges to obtain specific melt spinning process conditions. Typical but non-limiting melt spinning process conditions can be:

Spinning conditions		Index parameters
Product specifications		1.2D × 25 mm
Spinning speed		1200 m/min
Melting temperature		260°C
Screw extrusion pressure		7.0MPa
Cooling air	Wind speed	0.3-0.5 m/min
	Wind temperature	20-30°C
	Humidity	70%

The present disclosure also provides a use of the modified hollow cotton as described in the first object, and the modified hollow cotton is used as a filler for a warmth retention product;

preferably, the warmth retention product is selected from the group consisting of quilts, pillows, cushions, clothes, sleeping bags and tents;

preferably, the clothes are selected from the group consisting of warmth retention shirts, thermal underwear, down jackets, down vests and down pants.

The preparation methods of the quilts, pillows, cushions, clothes, sleeping bags or tents, as well as the warmth retention shirts, thermal underwear, down jackets according to the present disclosure can be made reference to the preparation methods of the corresponding products of the related techinologies in the art, and no specific limitations are made thereto in the present disclosure, and even the processes for preparing the corresponding products through the unmodified hollow cotton in the art can be made reference to.

The present disclosure also provides a use of the modified polyamide fiber as described in the first object, and the modified polyamide fiber is used as any one of knitwears, medical supplies and outdoor products.

Preferably, the modified polyamide fiber is used as a polyamide sock, a polyamide gauze kerchief, a mosquito net, a polyamide lace, a stretch polyamide garment, a polyamide silk or an interlaced silk fabric.

Preferably, the modified polyamide fiber is used for blending with wool products of wool or other chemical fiber to make materials for clothing.

Preferably, the modified polyamide fiber is used as cord thread, industrial fabrics, cable, conveyor belt, tent, fishing net or fishing line.

A polyamide fabric is woven or blended from the modified polyamide fiber as described in the first object.

A polyamide sock is woven or blended from the modified polyamide fiber as described in the first object.

Compared with the prior art, the present disclosure has the following beneficial effects:

(1) by means of a physical method, uniform dispersion of graphene in a hollow cotton is realized in the present disclosure, the technology is simple, a dispersing agent is not needed, and industrial production is easy;

(2) by means of a physical method, uniform dispersion of graphene in a polyamide fiber is realized in the present disclosure, the technology is simple, a dispersing agent is not needed, and industrial production is easy; and the spinning process of the modified polyamide fiber of the present disclosure is the same with that of the existing polyamide fiber, without needing any change, and both the spinning time

and the spinning length can reach the spinning requirements of the existing unmodified polyamide fiber;

(3) by introducing graphene into hollow cotton, and particularly introducing biomass graphene into the hollow cotton, the modified hollow cotton is enabled to have a low-temperature far infrared function, the far infrared normal emissivity thereof is 0.85 or more; the antibacterial performance is 90% or more, and the thermal insulation performance and the air permeability are both excellent. When the content of the biomass graphene is 1.4%, the thermal insulation rate is about 90% which is equivalent to that of white duck down with a down content of 90%, but the air permeability is about 240 mm/s which is far higher than that of the duck down.

(4) by introducing graphene into the polyamide fiber, and particularly introducing biomass graphene into the polyamide fiber, the modified polyamide fiber is enabled to have a low-temperature far infrared function, the far infrared normal emissivity thereof is 0.85 or more; the antibacterial performance is 90% or more.

Detail Description

The technical solutions of the present disclosure will be further described below by way of specific embodiments.

It will be apparent to those skilled in the art that the examples are merely illustrations of the present disclosure and should not be construed as specific limitations to the present disclosure.

Preparation Example 1 of graphene (redox graphene)

The method of Example 1 in the patent with publication number CN105217621A was used, which specifically included the following steps:

(A) in a reactor, reacting 2 g of graphite powder with a mixed system of 3 g of potassium dithionate, 3 g of phosphorus pentoxide, and 12 mL of concentrated sulfuric acid, and stirring at 80°C in a water bath for 4 hours until a dark blue solution was formed, the dark blue solution was cooled, suction filtered, and dried to obtain pre-oxidized graphite;

(B) weighing 2 g of the graphite oxide obtained in step (A) into a three-necked flask, adding 150 g of concentrated sulfuric acid solution under an ice-water bath condition, gradually adding 25 g of potassium permanganate, and stirring for 2 hours;

(C) transferring the three-necked flask of the above step (B) to an oil bath, raising the temperature to 35°C, and stirring for 2 hours, then adding a mixed solution of 30 wt % hydrogen peroxide and deionized water in an amount of 1:15 by volume with continuous stirring; the mixture was suction filtered, and washed with 4 mL of dilute hydrochloric acid with 10% mass fraction and deionized water once, respectively, then centrifuged, and dried to obtain first oxidized graphene oxide;

(D) mixing 2 g of graphene oxide prepared in step (C) again with 50 mL of concentrated sulfuric acid solution in a three-necked flask under an ice-water bath condition, then gradually adding 8 g of $KMnO_4$ thereto, followed by stirring for 1 hour;

(E) transferring the three-necked flask of the above step (D) to an oil bath, raising the temperature to 40°C and stirring for 1 hour, then continuously raising the temperature to 90°C and stirring for 1 hour, followed by adding a mixed solution of 30 wt % hydrogen peroxide and deionized water in an amount of 1:7 by volume with continuous stirring, the mixture was cooled after continuous stirring for 6 hours, then suction filtered, and washed with 4 mL of dilute hydrochloric acid with 10% mass fraction and deionized water twice, respectively, then centrifuged, and dried to obtain graphene oxide with uniform size.

Preparation Example 2 of graphene (biomass graphene)

The method of Example 10 in the patent with publication number CN104724696A was used, which specifically included the following steps:

Collecting straws, cutting them into small pieces after cleaned, which were then impregnated in an ethanol solution, the resulting solution was stirred at a constant speed of 100 r/min for 5 hours; then transferring the solution to a high-speed centrifuge with the rotation speed set at 3000 r/min, and centrifuging for 20 minutes, withdrawing smashed sample in the lower layer at the end. Under normal pressure and temperature, charging the smashed sample into a cell culture dish with a diameter of 15 cm, then placing the culture dish at the air inlet, and adjusting the flow parameters, with the wind speed set at 6 m/s and the air volume of 1400 m^3/h, and maintaining the ventilation state for 12 hours; heating a tube furnace to 1300°C, and introducing inert gas for protection, and maintaining for 30 minutes; placing the dried smashed sample into the tube furnace to heate 5 hours, graphene with distinct exfoliation was obtained after cooling to room temperature.

Preparation Example 3 of graphene (biomass graphene of a special source)

Preparation method of conventional cellulose, which specifically included the following steps:

(1) after wheat straws were smashed and pretreated, cooking the treated wheat straws by using an organic acid solution of formic acid and acetic acid having a total acid concentration of 80 wt%. The mass ratio of acetic acid to formic acid in the organic acid solution of this Example is 1:12, and before adding the raw materials, adding hydrogen peroxide (H_2O_2) in an amount of 1 wt% of the wheat straw raw materials as a catalyst, controlling the reaction temperature at 120°C to react for 30 minutes with a solid-liquid mass ratio of 1:10, and subjecting the resulting reaction solution to first solid-liquid separation;

(2) adding the solid obtained by the first solid-liquid separation to an organic acid

solution of formic acid and acetic acid having a total acid concentration of 75 wt% for acid washing, wherein hydrogen peroxide (H_2O_2) in an amount of 8 wt% of the wheat straw raw material was added to the organic acid solution having a total acid concentration of 75 wt% as a catalyst and the mass ratio of acetic acid to formic acid was 1:12, the temperature was controlled at 90°C, washed for 1 hour, the solid-liquid mass ratio was 1:9, and the reaction solution was subjected to second solid-liquid separation;

(3) collecting the liquid obtained by the first and second solid-liquid separations to be evaporated at high temperature and high pressure at 120°C and 301 kPa to dryness, condensing the obtained formic acid and acetic acid vapors back to the reaction kettle of step (1) as cooking liquor for the cooking in step (1);

(4) collecting the solid obtained by the second solid-liquid separation, and washing with water, wherein the temperature for water washing was controlled at 80°C, and the water washed pulp concentration was 6 wt%, then subjecting the water washed pulp to third solid-liquid separation;

(5) collecting the liquid obtained by the third solid-liquid separation, subjecting it to water and acid distillation, and recycling the resulting mixed acid solution to the reaction kettle of step (1) as cooking liquor for the cooking in step (1), and recycling the resulting water to step (5) for water washing;

(6) collecting the solid obtained by the third solid-liquid separation, and screening to obtain desired screened pulp cellulose.

Preparation of biomass graphene using cellulose as raw material:

(1) mixing cellulose and ferrous chloride in a mass ratio of 1: 1, stirring at 150°C and catalyzing for 4 hours, drying to the water content of the precursor to be 10 wt%, to obtain a precursor;

(2) heating the precursor to 170°C at a heating rate of 3°C/min under N_2 atmosphere, and maintaining the temperature for 2 hours, then heating by temperature programming to 400°C and maintaining the temperature for 3 hours, and then heating to 1200°C and maintaining the temperature for 3 hours to obtain a crude product; wherein the heating rate of the temperature programming was 15°C/min;

(3) washing the crude product with sodium hydroxide solution having a concentration of 10% and acid washing with hydrochloric acid having a concentration of 4 wt% at 55 to 65°C, and then water washing to obtain a biomass graphene.

By way of example, specifically, the hollow cotton was prepared by using PET as a raw material below:

Example A1

A hollow cotton, which was prepared by the following method:

(1) smashing PET blank polyester chips to an average particle size of 1 mm, so as to obtain PET blank polyester chip particles;

(2) mixing 1 kg of graphene powder (graphene powder obtained in Preparation Example 3 of graphene) and 9 kg of PET blank polyester chip particles, screw extruding at a melting temperature of 250°C, and drying in a vacuum drying oven to a moisture content of less than 300 ppm to obtain graphene-containing polyester masterbatches;

(3) uniformly mixing 1 kg of the graphene-containing polyester masterbatches with 1 kg of PET blank polyester chips, and then continuously adding 5 kg of PET blank polyester chips to mix uniformly;

(4) melting the material obtained in step (3), and then spinning, opening after

completing post spinning to obtain a polyester hollow cotton with a graphene content of 1.4 wt%.

Example A2

A hollow cotton, which differed from Example A1 in that:

(3) uniformly mixing 1 kg of the graphene-containing polyester masterbatches with 1 kg of PET blank polyester chips, and then continuously adding 3 kg of PET blank polyester chips to mix uniformly;

(4) melting the material obtained in step (3), and then spinning, opening after completing post spinning to obtain a polyester hollow cotton with a graphene content of 2 wt%.

Example A3

A hollow cotton, which differed from Example A1 in that:

(3) uniformly mixing 1 kg of the graphene-containing polyester masterbatches with 1 kg of PET blank polyester chips, and then continuously adding 8kg of PET blank polyester chips to mix uniformly;

(4) melting the material obtained in step (3), and then spinning, opening after completing post spinning to obtain a polyester hollow cotton with a graphene content of 1 wt%.

Example A4

A hollow cotton, which differed from Example A1 in that:

(3) uniformly mixing 1 kg of the graphene-containing polyester masterbatches with 4.5kg of PET blank polyester chips, and then continuously adding 45kg of PET

blank polyester chips to mix uniformly;

(4) melting the material obtained in step (3), and then spinning, opening after completing post spinning to obtain a polyester hollow cotton with a graphene content of 0.2 wt%.

Example A5

A hollow cotton, which differed from Example A1 in that:

Step (3') was performed after step (3): screw extruding the material obtained in step (3) at 250°C.

Example A6

A hollow cotton, which was prepared by the following method:

(1) smashing PET blank polyester chips to an average particle size of 1 mm, so as to obtain PET blank polyester chip particles;

(2) mixing 1 kg of graphene powder (graphene powder obtained in Preparation Example 3 of graphene) and 4kg of PET blank polyester chip particles, screw extruding at a melting temperature of 250°C, and drying in a vacuum drying oven to a moisture content of less than 300 ppm to obtain graphene-containing polyester masterbatches;

(3) uniformly mixing 1 kg of the graphene-containing polyester masterbatches with 1 kg of PET blank polyester chips, and then continuously adding 4.7 kg of PET blank polyester chips to mix uniformly;

(4) melting the material obtained in step (3), and then spinning, opening after completing post spinning to obtain a polyester hollow cotton with a graphene content of 3 wt%.

Example A7

A hollow cotton, which differed from Example A6 in that:

(3) uniformly mixing 1 kg of the graphene-containing polyester masterbatches with 1 kg of PET blank polyester chips, and then continuously adding 2kg of PET blank polyester chips to mix uniformly;

(4) melting the material obtained in step (3), and then spinning, opening after completing post spinning to obtain a polyester hollow cotton with a graphene content of 5 wt%.

Example A8

A hollow cotton, which differed from Example A6 in that:

(3) uniformly mixing 1 kg of the graphene-containing polyester masterbatches with 0.5kg of PET blank polyester chips, and then continuously adding 0.5kg of PET blank polyester chips to mix uniformly;

(4) melting the material obtained in step (3), and then spinning, opening after completing post spinning to obtain a polyester hollow cotton with a graphene content of 10 wt%.

Example A9

A hollow cotton, which differed from Example A1 in that: the smashing step of step (1) was not performed, and 1 kg of graphene powder (graphene powder obtained from Preparation Example 3 of graphene) and 9 kg of PET blank polyester chips were directly mixed in step (2).

Example A10

A hollow cotton, which differed from Example A1 in that: 1 kg of the graphene-containing polyester masterbatches and 6 kg of PET blank polyester chips were directly mixed in step (3); and then step (4) was performed.

Example A11

A hollow cotton, which differed from Example A1 in that: the graphene powder obtained from Preparation Example 3 of graphene was replaced with the graphene powder obtained from Preparation Example 1 of graphene in step (2).

Example A12

A hollow cotton, which differed from Example A1 in that: the graphene powder obtained from Preparation Example 3 of graphene was replaced with the graphene powder obtained from Preparation Example 2 of graphene in step (2).

Comparative Example A1

Comparative Example A1 differed from Example A1 in that: the smashing step of step (1) was not performed, and 1 kg of graphene powder and 9 kg of PET blank polyester chips were directly mixed in step (2); and 1 kg of the graphene-containing polyester masterbatches and 6 kg of PET blank polyester chips were directly mixed uniformly in step (3); and then step (4) was performed.

Comparative Example A2

White duck down with a down content of 90% was used as Comparative Example A2.

Comparative Example A3

A hollow cotton, which was prepared by the following method:

(1) smashing the PET blank polyester chips to an average particle size of 1 mm, so as to obtain the PET blank polyester chip particles;

(2) melting the material obtained in step (1), and then spinning, opening after completing post spinning to obtain a polyester hollow cotton.

Performance tests

The polyester hollow cottons prepared by the Examples and Comparative Examples were tested as follows:

(1) Warmth retention rate: Test method GBT11048-2008 Textiles-Physiological effects-Measurement of thermal and water-vapour resistance under steady-state conditions;

(2) Air permeability: Test method GBT5453-1997 Textiles--Determination of the permeability of fabrics to air;

(3) Far infrared normal emissivity: The far infrared normal emissivity is tested according to FZ/T64010-2000 Test Method by National Textiles Supervision Testing Center;

(4) Bacteria inhibition property: Bacteria inhibition property is tested according to GB/T20944.3-2008 Test Method by National Textiles Supervision Testing Center, exemplified by Staphylococcus aureus;

The test results were shown in Table 1:

Table 1-1 Performance Test Results of Examples A1-A9

Test items	Examples								
	A1	A2	A3	A4	A5	A6	A7	A8	A9
Warmth retention rate (%)	90.03	90.73	89.50	85.21	89.83	91.05	89.98	82.10	88.03
Air permeability (mm/s)	232.4	238.2	227.3	210.3	231.4	238.3	238.4	230.12	230.1
Far infrared normal emissivity (%)	0.89	0.89	0.88	0.85	0.89	0.90	0.92	0.88	0.87
Bacteria inhibition property (%)	95	95	95	93	95	99	99	90	92

Table 1-2 Performance Test Results of Examples 10-12 and Comparative Examples

Test items	Examples			Comparative Examples		
	A10	A11	A12	A1	A2	A3
Warmth retention rate (%)	88.12	84.12	87.16	80.20	90.67	77.17
Air permeability (mm/s)	229.5	200.3	222.4	236.3	57.6	241.1
Far infrared normal emissivity (%)	0.87	0.80	0.82	0.80	0.72	0.70
Bacteria inhibition property (%)	93	66	80	80	10	10

By way of example, specifically, modified polyamide fiber was prepared by using PA-6 and PA-66 as raw materials:

Example B1

A modified polyamide fiber, which was prepared by the following method:

(1) smashing blank PA-6 chips to an average particle size of 1 mm, so as to obtain blank PA-6 chip particles;

(2) mixing 1 kg of graphene powder (graphene powder obtained in Preparation Example 3 of graphene) and 9 kg of blank PA-6 chip particles, screw extruding at a melting temperature of 220°C, and drying in a vacuum drying oven to a moisture content of less than 300 ppm to obtain graphene-containing PA-6 masterbatches;

(3) uniformly mixing 1 kg of the graphene-containing PA-6 masterbatches with 1 kg of blank PA-6 chips, and then continuously adding 5 kg of blank PA-6 chips to mix uniformly;

(4) melting the material obtained in step (3), and then spinning, modified PA-6 fiber with a graphene content of 1.4 wt% was obtained after completing post spinning, which could be spun normally for 8 hours without yarn breaking.

Example B2

A modified polyamide fiber, which differed from Example B1 in that:

(3) uniformly mixing 1 kg of the graphene-containing PA-6 masterbatches with 1 kg of blank PA-6 chips, and then continuously adding 3 kg of blank PA-6 chips to mix uniformly;

(4) melting the material obtained in step (3), and then spinning, modified PA-6 fiber with a graphene content of 2 wt% was obtained after completing post spinning, which could be spun normally for 8 hours without yarn breaking.

Example B3

A modified polyamide fiber, which differed from Example B1 in that:

(3) uniformly mixing 1 kg of the graphene-containing PA-6 masterbatches with 1 kg of blank PA-6 chips, and then continuously adding 8kg of blank PA-6 chips to mix uniformly;

(4) melting the material obtained in step (3), and then spinning, modified PA-6 fiber with a graphene content of 1 wt% was obtained after completing post spinning, which could be spun normally for 8 hours without yarn breaking.

Example B4

A modified polyamide fiber, which differed from Example B1 in that:

(3) uniformly mixing 1 kg of the graphene-containing PA-6 masterbatches with 4.5kg of blank PA-6 chips, and then continuously adding 45kg of blank PA-6 chips to mix uniformly;

(4) melting the material obtained in step (3), and then spinning, modified PA-6 fiber with a graphene content of 0.2 wt% was obtained after completing post spinning, which could be spun normally for 8 hours without yarn breaking.

Example B5

A modified polyamide fiber, which differed from Example B1 in that:

Step (3') was performed after step (3): screw extruding the material obtained in step (3) at 210°C.

Example B6

A modified polyamide fiber, which was prepared by the following method:

(1) smashing blank PA-66 chips to an average particle size of 1 mm, so as to obtain blank PA-66 chip particles;

(2) mixing 1 kg of graphene powder (graphene powder obtained in Preparation Example 3 of graphene) and 4 kg of blank PA-66 chip particles, screw extruding at a melting temperature of 240°C, and drying in a vacuum drying oven to a moisture content of less than 300 ppm to obtain graphene-containing PA-66 masterbatches;

(3) uniformly mixing 1 kg of the graphene-containing PA-66 masterbatches with 1 kg of blank PA-66 chips, and then continuously adding 4.7 kg of blank PA-66 chips to mix uniformly;

(4) melting the material obtained in step (3), and then spinning, modified PA-66 fiber with a graphene content of 3 wt% was obtained after completing post spinning, which could be spun normally for 8 hours without yarn breaking.

Example B7

A modified polyamide fiber, which differed from Example B6 in that:

(3) uniformly mixing 1 kg of the graphene-containing PA-66 masterbatches with 1 kg of blank PA-66 chips, and then continuously adding 2 kg of blank PA-66 chips to mix uniformly;

(4) melting the material obtained in step (3), and then spinning, modified PA-66 fiber with a graphene content of 5 wt% was obtained after completing post spinning, which could be spun normally for 8 hours without yarn breaking.

Example B8

A modified polyamide fiber, which differed from Example B6 in that:

(3) uniformly mixing 1 kg of the graphene-containing PA-66 masterbatches with 0.5kg of blank PA-66 chips, and then continuously adding 0.5kg of blank PA-66 chips to mix uniformly;

(4) melting the material obtained in step (3), and then spinning, modified PA-66 fiber with a graphene content of 10 wt% was obtained after completing post spinning, which could be spun normally for 8 hours without yarn breaking.

Example B9

A modified polyamide fiber, which differed from Example B1 in that: the smashing step of step (1) was not performed, and 1 kg of graphene powder (graphene powder obtained from Preparation Example 3 of graphene) and 9 kg of blank PA-66 chips were directly mixed in step (2), which could be spun normally for 8 hours without yarn breaking.

Example B10

A modified polyamide fiber, which differed from Example B1 in that: 1 kg of the graphene-containing PA-66 masterbatches and 6 kg of blank PA-66 chips were directly mixed uniformly in step (3); and then step (4) was performed.

Example B11

A modified polyamide fiber, which differed from Example B1 in that: the graphene powder obtained from Preparation Example 3 of graphene was replaced with the graphene powder obtained from Preparation Example 1 of graphene in step (2).

Example B12

A modified polyamide fiber, which differed from Example B1 in that: the graphene powder obtained from Preparation Example 3 of graphene was replaced with the graphene powder obtained from Preparation Example 2 of graphene in step (2).

Comparative Example B1

Comparative Example B1 differed from Example B1 in that: the smashing step of step (1) was not performed, and 1 kg of graphene powder and 9 kg of blank PA-6 chips were directly mixed in step (2); and 1 kg of the graphene-containing PA-6 masterbatches and 6 kg of blank PA-6 chips were directly mixed uniformly in step (3); and then step (4) was performed.

Comparative Example B2

A polyamide fiber, which was prepared by the following method:

(1) smashing blank PA-6 chips to an average particle size of 1 mm, so as to obtain blank PA-6 chip particles;

(2) melting the material obtained in step (1), and then spinning, PA-6 fiber was obtained after completing post spinning.

Performance testS

The modified polyamide fibers and the polyamide fibers prepared by the Examples and Comparative Examples were tested as follows:

(1) Breaking strength and elongation at break: Breaking strength and elongation at break were tested according to the test method of GB/T 3923.1-1997 Testiles-Determination of breaking force and elongation at breaking force;

(2) Air permeability: Test method GBT5453-1997 Textiles--Determination of the permeability of fabrics to air;

(3) Far infrared normal emissivity: The far infrared normal emissivity is tested according to FZ/T64010-2000 Test Method by National Textiles Supervision Testing Center;

(4) Bacteria inhibition property: Bacteria inhibition property is tested according to GB/T20944.3-2008 Test Method by National Textiles Supervision Testing Center,

exemplified by Staphylococcus aureus;

The test results were shown in Table 2:

Table 2-1 Performance Test Results of Examples 1-9

Test items	Examples								
	B1	B2	B3	B4	B5	B6	B7	B8	B9
Breaking strength (N/tex)	56	56	55	55	55	56	57	56	56
Elongation at break (%)	60	63	56	55	60	64	65	62	58
Air permeability (mm/s)	232.4	238.2	227.3	210.3	231.4	238.3	238.4	230.12	230.1
Far infrared normal emissivity (%)	0.89	0.89	0.88	0.85	0.89	0.90	0.92	0.88	0.87
Bacteria inhibition property (%)	95	95	95	93	95	99	99	90	92
Spinning time	≥8h	≥8h	≥8h	≥8h	≥8h	≥8h	≥8h	≥8h	≥8h

Table 2-2 Performance Test Results of Examples 10-12 and Comparative Examples

Test items	Examples			Comparative Examples	
	B10	B11	B12	B1	B3
Breaking strength (N/tex)	55	54	55	20	64
Elongation at break (%)	60	56	62	5	65
Air permeability (mm/s)	229.5	200.3	222.4	236.3	241.1
Far infrared normal emissivity (%)	0.87	0.80	0.82	0.80	0.70
Bacteria inhibition property (%)	93	66	80	80	10
Spinning time	≥8h	≥8h	≥8h	Break at 1 hour	≥8h

Applicant has stated that although the process methods of the present disclosure have been described by the above Examples in the present disclosure, the present disclosure is not limited thereto, that is to say, it is not meant that the present disclosure has to be implemented depending on the above process methods. It will be apparent to those skilled in the art that any improvements made to the present disclosure, equivalent replacements and addition of adjuvant ingredients to the raw materials selected in the present disclosure, and selections of the specific implementations, etc., all fall within the protection scope and the disclosure scope of the present disclosure.

Claims

What is claimed is:

1. A modified fiber, wherein the modified fiber is doped with graphene;
the modified fiber comprises any one of modified hollow cotton or modified polyamide fiber;

wherein the preparation method of the modified hollow cotton comprises the following steps:

(A'-1) mixing graphene with blank polyester chips, screw extruding, and drying to obtain graphene-containing polyester masterbatches;

(A'-2) uniformly mixing the graphene-containing polyester masterbatches with a portion of blank polyester chips, and then mixing with the remaining blank polyester chips b;

(A'-3) melt spinning the resulting materials, and then opening to obtain the modified hollow cotton;

the preparation method of the modified polyamide fiber comprises the following steps:

(B'-1) mixing graphene with blank polyamide chips, screw extruding, and drying to obtain graphene-containing polyamide masterbatches;

(B'-2) uniformly mixing the graphene-containing polyamide masterbatches with a portion of blank polyamide chips, and then mixing with the remaining blank polyamide chips b;

(B'-3) melt spinning the resulting materials to obtain the modified polyamide fiber;
or,

wherein the preparation method of the modified hollow cotton comprises the following steps:

(A-1) smashing blank polyester chip to obtain blank polyester chip particles;

(A-2) mixing graphene with blank polyester chip particles, screw extruding, and drying to obtain graphene-containing polyester masterbatches;

(A-3) uniformly mixing the graphene-containing polyester masterbatches with the blank polyester chips;

(A-4) melt spinning the resulting materials, and then opening to obtain the modified hollow cotton;

the preparation method of the modified polyamide fiber comprises the following steps:

(B-1) smashing blank polyamide chips to obtain blank polyamide chip particles;

(B-2) mixing graphene with blank polyamide chip particles, screw extruding, and drying to obtain graphene-containing polyamide masterbatches;

(B-3) uniformly mixing graphene-containing polyamide masterbatches with the blank polyamide chips;

(B-4) melt spinning the resulting materials to obtain the modified polyamide fiber.

2. The modified fiber of claim 1, wherein the graphene is a biomass graphene.

3. The modified fiber of claim 2, wherein the biomass graphene is prepared from biomass.

4. The modified fiber of claim 2, wherein the biomass graphene is prepared from

biomass-derived cellulose.

5. The modified fiber of claim 2, wherein the biomass is any one selected from the group consisting of agricultural and forestry wastes, plants, and a combination of at least two selected therefrom.

6. The modified fiber of claim 5, wherein the plants are any one selected from the group consisting of coniferous wood, broadleaf wood, and a combination of at least two selected therefrom.

7. The modified fiber of claim 5, wherein the agricultural and forestry wastes are any one selected from the group consisting of corn stalks, corn cobs, sorghum stalks, beet residues, bagasse, furfural residues, xylose residues, wood chips, cotton stalks, shells, reeds, and a combination of at least two selected therefrom.

8. The modified fiber of claim 7, wherein the agricultural and forestry wastes are corn cobs.

9. The modified fiber of any one of claims 1-8, wherein the doping amount of graphene in the modified hollow cotton is 0.2-10 wt%.

10. The modified fiber of any one of claims 1-8, wherein the doping amount of graphene in the modified polyamide fiber is 0.2-10 wt%.

11. The modified fiber of any one of claims 1-10, wherein the far infrared detection normal emissivity of the modified hollow cotton is greater than 0.85.

12. The modified fiber of any one of claims 1-10, wherein the far infrared detection normal emissivity of the modified polyamide fiber is greater than 0.85.

13. A preparation method of the modified fiber of any one of claims 1-12, wherein the preparation method of the modified hollow cotton comprises the following steps:

(A'-1) mixing graphene with blank polyester chips, screw extruding, and drying to obtain graphene-containing polyester masterbatches;

(A'-2) uniformly mixing the graphene-containing polyester masterbatches with a portion of blank polyester chips, and then mixing with the remaining blank polyester chips b;

(A'-3) melt spinning the resulting materials, and then opening to obtain the modified hollow cotton;

the preparation method of the modified polyamide fiber comprises the following steps:

(B'-1) mixing graphene with blank polyamide chips, screw extruding, and drying to obtain graphene-containing polyamide masterbatches;

(B'-2) uniformly mixing the graphene-containing polyamide masterbatches with a portion of blank polyamide chips, and then mixing with the remaining blank polyamide chips b;

(B'-3) melt spinning the resulting materials to obtain the modified polyamide fiber.

14. The preparation method of claim 13, wherein the blank polyester chips of step (A'-1) and step (A'-2) are PET and/or PBT.

15. The preparation method of claim 13, wherein the blank polyester chips of step (A'-1) are PET.

16. The preparation method of claim 13, wherein the graphene content in the graphene-containing polyester masterbatches is 1-20 wt%.

17. The preparation method of claim 13, wherein the melting temperature of the screw extrusion of step (A'-1) is 230-270°C.

18. The preparation method of claim 13, wherein the moisture content of the graphene-containing polyester masterbatches is 600 ppm or less;

the blank polyamide chips of step (B'-1) and step (B'-2) are any one of PA-6, PA-66, PA-610, PA-1010, and MCPA.

19. The preparation method of claim 13, wherein the graphene content in the graphene-containing polyamide masterbatches is 3-10 wt%.

20. The preparation method of claim 13, wherein the melting temperature of the screw extrusion of step (B'-1) is 210-240°C.

21. The preparation method of claim 13, wherein the moisture content of the graphene-containing polyamide masterbatches is 600 ppm or less.

22. The preparation method of claim 13 or 14, wherein the mass ratio of the graphene-containing polyester masterbatches to the blank polyester chips in step (A'-2) is 1:(5-30).

23. The preparation method of claim 13 or 14, wherein in step (A'-2), the ratio of the part of the blank polyester chips to the integral blank polyester chip added in step (A'-2) is 1:(2-10).

24. The preparation method of claim 13 or 14, wherein the mass ratio of the graphene-containing polyamide masterbatches to the blank polyamide chips in step (B'-2) is 1:(5-30).

25. The preparation method of claim 13 or 14, wherein in step (B'-2), the ratio of the part of the blank polyamide chips to the integral blank polyamide chips added in step (B'-2) is 1:(2-10).

26. The preparation method of any one of claims 13-25, wherein the intrinsic

viscosity of the raw materials for melt spinning in step (A'-3) is 0.60 dL/g or more.

27. The preparation method of any one of claims 13-25, wherein the intrinsic viscosity of the raw materials for melt spinning in step (B'-3) is 3 dL/g or less.

28. The preparation method of any one of claims 13-27, wherein step (A'-2') is set between step (A'-4) and step (A'-3): screw extruding the materials uniformly mixed in step (A'-2) again.

29. The preparation method of any one of claims 13-27, wherein the melting temperature of the screw extrusion of step (A'-2') is 230-270°C.

30. The preparation method of any one of claims 13-27, wherein step (B'-2') is set between step (B'-2) and step (B'-3): screw extruding the materials uniformly mixed in step (B'-2) again.

31. The preparation method of any one of claims 13-27, wherein the melting temperature of the screw extrusion of step (B'-2') is 210-240°C.

32. The preparation method of any one of claims 13-31, wherein step (A'-1') is performed before step (A'-1): smashing blank polyester chips into blank polyester chip particles for mixing with the graphene of step (A'-1).

33. The preparation method of any one of claims 13-31, wherein the particle size of the blank polyester chip particles of step (A'-1') is 3 mm or less.

34. The preparation method of any one of claims 13-31, wherein step (B'-1') is performed before step (B'-1): smashing blank polyamide chips into blank polyamide chip particles for mixing with the graphene of step (B'-1).

35. The preparation method of any one of claims 13-31, wherein the particle size of the blank polyamide chip particles of step (B'-1') is 3 mm or less.

36. A preparation method of the modified fiber of any one of claims 1-12, wherein the preparation method of the modified hollow cotton comprises the following steps:

(A-1) smashing blank polyester chip to obtain blank polyester chip particles;

(A-2) mixing graphene with blank polyester chip particles, screw extruding, and drying to obtain graphene-containing polyester masterbatches;

(A-3) uniformly mixing the graphene-containing polyester masterbatches with the blank polyester chips;

(A-4) melt spinning the resulting materials, and then opening to obtain the modified hollow cotton;

the preparation method of the modified polyamide fiber comprises the following steps:

(B-1) smashing blank polyamide chips to obtain blank polyamide chip particles;

(B-2) mixing graphene with blank polyamide chip particles, screw extruding, and drying to obtain graphene-containing polyamide masterbatches;

(B-3) uniformly mixing graphene-containing polyamide masterbatches with the blank polyamide chips;

(B-4) melt spinning the resulting materials to obtain the modified polyamide fiber.

37. The preparation method of claim 36, wherein the particle sizes of the blank polyester chip particles and the blank polyamide chip particles are 3 mm or less.

38. The preparation method of claim 36, wherein the blank polyester chips of step (A-1) and step (A-3) are PET and/or PBT.

39. The preparation method of claim 36, wherein the blank polyester chips of step (A-1) are PET.

40. The preparation method of claim 36, wherein the blank polyamide chips of step (B-1) and step (B-3) are any one of PA-6, PA-66, PA-610, PA-1010, and MCPA.

41. The preparation method of claim 36 or 37, wherein the graphene content in the graphene-containing polyester masterbatches is 1-20 wt%.

42. The preparation method of claim 36 or 37, wherein the graphene content in the graphene-containing polyamide masterbatches is 3-10 wt%.

43. The preparation method of claim 36 or 37, wherein the melting temperature of the screw extrusion of step (A-2) is 230-270°C.

44. The preparation method of claim 36 or 37, wherein the melting temperature of the screw extrusion of step (B-2) is 210-240°C.

45. The preparation method of claim 36 or 37, wherein the moisture content of the graphene-containing polyester masterbatches is 600 ppm or less.

46. The preparation method of claim 36 or 37, wherein the moisture content of the graphene-containing polyamide masterbatches is 600 ppm or less.

47. The preparation method of any one of claims 36-46, wherein the mass ratio of the graphene-containing polyester masterbatches to the blank polyester chips in step (A-3) is 1:(5-30).

48. The preparation method of any one of claims 36-46, wherein the mass ratio of the graphene-containing polyamide masterbatches to the blank polyamide chips in step (B-3) is 1:(5-30).

49. The preparation method of any one of claims 36-48, wherein the intrinsic

viscosity of the raw materials for melt spinning in step (A-4) is 0.60 dL/g or more.

50. The preparation method of any one of claims 36-48, wherein the intrinsic viscosity of the raw materials for melt spinning in step (B-4) is 3 dL/g or less.

51. A use of the modified hollow cotton of any one of claims 1-12, wherein the modified hollow cotton is used as a filler for a warmth retention product.

52. The use of claim 51, wherein the warmth retention product is selected from the group consisting of quilts, pillows, cushions, clothes, sleeping bags and tents.

53. The use of claim 52, wherein the clothes are selected from the group consisting of warmth retention shirts, thermal underwear, down jackets, down vests and down pants.

54. A use of the modified polyamide fiber of any one of claims 1-12, wherein the modified polyamide fiber is used as any one of knitwears, medical supplies and outdoor products.

55. The use of claim 54, wherein the modified polyamide fiber is used as a polyamide sock, a polyamide gauze kerchief, a mosquito net, a polyamide lace, a stretch polyamide garment, a polyamide silk or an interlaced silk fabric.

56. The use of claim 54, wherein the modified polyamide fiber is used for blending with wool products of wool or other chemical fiber to make materials for clothing.

57. The use of claim 54, wherein the modified polyamide fiber is used as cord thread, industrial fabrics, cable, conveyor belt, tent, fishing net or fishing line.