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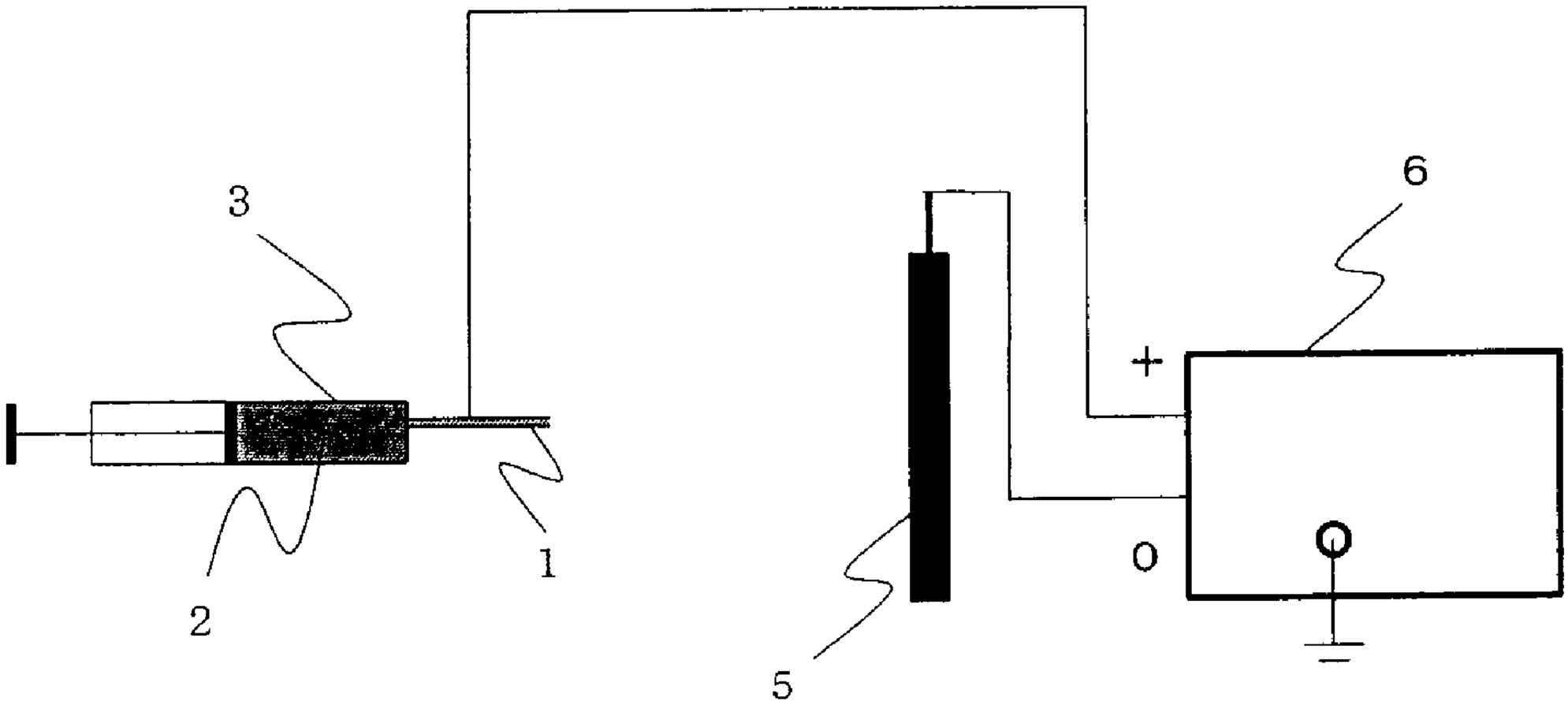
(54) Title: EXTREMELY FINE POLYLACTIC ACID FIBER, FIBROUS STRUCTURE AND PROCESS FOR PRODUCING THESE



(57) Abrégé/Abstract:
A fibrous structure obtained by spinning a solution of L-lactic acid condensation product and D-lactic acid condensation product in accordance with an electrostatic spinning technique. There can be provided a fibrous structure containing fibers that have an extremely small fiber diameter, exhibiting excellent heat resistance and biodegradability.

ABSTRACT

A fiber structure is obtained by spinning of a solution of an L-lactic acid condensate and a D-lactic acid condensate by electrospinning. It is possible to provide a fiber structure comprising fibers with extremely small fiber diameters, as well as excellent heat resistance and biodegradability.

DESCRIPTION

ULTRAFINE POLYLACTIC ACID FIBERS AND FIBER STRUCTURE, AND PROCESS FOR THEIR PRODUCTION

Technical Field

The present invention relates to fibers comprising biodegradable polylactic acid as a constituent component, and more specifically it relates to ultrafine polylactic acid fibers and a fiber structure, and to a process for their production.

Background Art

Ultrafine fibers have a soft feel and are therefore used for such purposes as woven and knitted fabrics or artificial leather, for clothing or interior goods.

They are also used in the forms of sheets or nonwoven fabrics for such purposes as filters, insulating sheets, wipers, packing materials, sanitary goods and the like.

In recent years it has been desirable to reduce environmental load from the standpoint of preserving the earth environment. Yet because 6-nylon, polyethylene terephthalate, polypropylene and the like used for conventional ultrafine fibers do not decompose in soil or compost, they must be incinerated or buried after use and therefore create a major environmental load due to atmospheric pollution or prolonged durability after burial.

A demand therefore exists for ultrafine fibers that decompose in soil or compost. For example, there have been proposed ultrafine fibers composed of a biodegradable thermoplastic aliphatic polyester with a single fiber

diameter of no greater than 0.5 decitex (for example, see Patent document 1). There have also been proposed fibers composed of poly(L-lactic acid) with a fiber diameter of 100 nm-4 μm (for example, see Patent document 2).

However, the ultrafine fibers referred to above have poor heat resistance and their uses have therefore been limited.

A method for improving the heat resistance of polylactic acid that has been of note recently is stereo complex formation with poly(L-lactic acid) and poly(D-lactic acid) (for example, see Patent document 3).

It is known that blending poly(L-lactic acid) and poly(D-lactic acid) in equivalent amounts can yield racemic crystals with a higher melting point than polylactic acid.

However, hitherto obtained polylactic acid stereo complex fibers are mixtures of poly(L-lactic acid) single crystals and poly(D-lactic acid) single crystals, and their heat resistance has been insufficient. Such fibers have large fiber diameters and the fiber structures formed from the fibers have exhibited inadequate flexibility (for example, see Patent documents 3 and 4).

[Patent document 1] Japanese Unexamined Patent Publication No. 2001-192932

[Patent document 2] International Patent Publication No. 02/16680

[Patent document 3] Japanese Unexamined Patent Publication No. 2002-30523

[Patent document 4] Japanese Unexamined Patent Publication No. 2003-138437

Disclosure of the Invention

It is an object of the present invention to overcome the aforementioned problems of the prior art by providing fibers with a very small fiber diameter, and excellent heat resistance and biodegradability.

It is another object of the invention to provide a fiber structure containing the fibers.

It is yet another object of the invention to provide a process for production of the fiber structure by a very convenient method.

Brief Explanation of the Drawings

Fig. 1 is a schematic view showing an embodiment of the construction of an apparatus for production of a fiber structure of the invention.

Fig. 2 is a schematic view showing an embodiment of the construction of an apparatus for production of a fiber structure of the invention.

Fig. 3 is a photograph of the surface of the fiber structure obtained in Example 1, taken with a scanning electron microscope (2000x).

Fig. 4 is a photograph of the surface of the fiber structure obtained in Example 1, taken with a scanning electron microscope (8000x).

Fig. 5 is a photograph of the surface of the fiber structure obtained in Example 2, taken with a scanning electron microscope (2000x).

Fig. 6 is a photograph of the surface of the fiber structure obtained in Example 2, taken with a scanning electron microscope (8000x).

Fig. 7 is a photograph of the surface of the fiber structure obtained in Comparative Example 1, taken with a

scanning electron microscope (2000x).

Fig. 8 is a photograph of the surface of the fiber structure obtained in Comparative Example 1, taken with a scanning electron microscope (8000x).

Fig. 9 is a photograph of the surface of the fiber structure obtained in Comparative Example 2, taken with a scanning electron microscope (2000x).

Fig. 10 is a photograph of the surface of the fiber structure obtained in Comparative Example 2, taken with a scanning electron microscope (8000x).

Fig. 11 is a photograph of the surface of the fiber structure obtained in Comparative Example 3, taken with a scanning electron microscope (2000x).

Fig. 12 is a photograph of the surface of the fiber structure obtained in Comparative Example 3, taken with a scanning electron microscope (8000x).

Fig. 13 is a photograph of the surface of the fiber structure obtained in Example 3, taken with a scanning electron microscope (2000x).

Fig. 14 is a photograph of the surface of the fiber structure obtained in Example 3, taken with a scanning electron microscope (8000x).

Fig. 15 is a photograph of the surface of the fiber structure obtained in Example 4, taken with a scanning electron microscope (2000x).

Fig. 16 is a photograph of the surface of the fiber structure obtained in Example 4, taken with a scanning electron microscope (8000x).

Fig. 17 is a photograph of the surface of the fiber structure obtained in Comparative Example 4, taken with a scanning electron microscope (2000x).

Fig. 18 is a photograph of the surface of the fiber structure obtained in Comparative Example 4, taken with a scanning electron microscope (8000x).

Fig. 19 is a photograph of the surface of the fiber structure obtained in Comparative Example 5, taken with a scanning electron microscope (2000x).

Fig. 20 is a photograph of the surface of the fiber structure obtained in Comparative Example 5, taken with a scanning electron microscope (8000x).

Fig. 21 is a photograph of the surface of the fiber structure obtained in Comparative Example 6, taken with a scanning electron microscope (2000x).

Fig. 22 is a photograph of the surface of the fiber structure obtained in Comparative Example 6, taken with a scanning electron microscope (8000x).

Best Mode for Carrying Out the Invention

The invention will now be explained in greater detail.

The fibers of the invention must have a mean fiber diameter of no greater than 10 μm. The mean fiber diameter of the fibers preferably does not exceed 10 μm because the obtained fiber structure will lack flexibility. The mean fiber diameter of the fibers is preferably in the range of 0.01-5 μm.

The fibers of the invention also must have fiber lengths of 20 μm or greater. If the fiber lengths are less than 20 μm, the dynamic strength of the obtained fiber structure will be insufficient. The fiber lengths are preferably at least 40 μm and more preferably at least 1 mm.

The fibers of the invention must have as the main

constituent component a polylactic acid component with a melting point of 190°C or higher, and they contain substantially no constituent component with a melting point of below 190°C.

Here, "contain substantially no constituent component with a melting point of below 190°C" means that no endothermic peak is exhibited at below 190°C in the melting endotherm (DSC curve) upon differential scanning calorimetric analysis of the obtained fibers.

Preferably no constituent component with a melting point of below 190°C is present because heat resistance will be lacking. The melting point of the fiber component is more preferably 195°C-250°C.

As mentioned above, the fibers of the invention have as the main constituent component a polylactic acid component with a melting point of 190°C or higher.

The fibers of the invention more preferably have surface depressions with diameters of 0.01-1 μm, with the depressions constituting 10-95% of the fiber surfaces. This kind of surface structure will increase the surface area of fibers structures formed from the fibers, thereby improving the rate of decomposition in soil or compost. The diameters of the depressions are more preferably 0.02-0.5 μm, and the proportion of depressions on the fiber surfaces is more preferably 40-95%.

According to the invention, the polylactic acid component is a polymer comprising a condensate with at least 80 mol% lactic acid based on the total repeating units, and it may be copolymerized with other components so long as the features of the invention are not prevented.

"Main constituent component" means that the component

constitutes at least 75 wt%, preferably at least 80 wt%, more preferably at least 90 wt% and most preferably at least 95 wt% based on the total constituent components of the fibers of the invention.

According to the invention, the polylactic acid component preferably consists of a mixture of a condensate with at least 80 mol% L-lactic acid based on the total repeating units and a condensate with at least 80 mol% D-lactic acid based on the total repeating units.

Here, a condensate with at least 80 mol% L-lactic acid based on the total repeating units means a content of 80-100 mol% L-lactic acid and 0-20 mol% of D-lactic acid or a copolymerizing component other than D-lactic acid. On the other hand, a condensate with at least 80 mol% D-lactic acid based on the total repeating units means a content of 80-100 mol% D-lactic acid and 0-20 mol% of L-lactic acid or a copolymerizing component other than L-lactic acid.

As copolymerizing components other than D-lactic acid and L-lactic acid there may be mentioned oxy acids, lactones, dicarboxylic acids and polyhydric alcohols. There may also be mentioned various polyesters, polyethers and polycarbonates comprising such components and having ester bond-forming functional groups.

According to the invention, the polylactic acid component is preferably a mixture comprising a condensate with at least 80 mol% L-lactic acid based on the total repeating units and a condensate with at least 80 mol% D-lactic acid based on the total repeating units, in a weight ratio of (6:4)-(4:6).

More preferably, the condensate with at least 80 mol% L-lactic acid based on the total repeating units and the

condensate with at least 80 mol% D-lactic acid based on the total repeating units are mixed in substantially a 5:5 ratio.

According to the invention, the weight-average molecular weight of the polylactic acid component is more preferably 100,000 or greater for improved dynamic strength of the obtained fiber structure.

The fiber structure of the invention includes at least the aforementioned ultrafine polylactic acid fibers, but a "fiber structure" according to the invention may be any three-dimensional structure formed by weaving, knitting or laminating the fibers, and a nonwoven fabric may be mentioned as a preferred example.

The content of the ultrafine polylactic acid fibers in the fiber structure of the invention is not particularly limited, but the features of the ultrafine polylactic acid fibers can be exhibited with a content of 50 wt% or greater. The content is more preferably 80 wt% or greater, and even more preferably the fiber structure is composed essentially of the polylactic acid fibers alone.

In particular, preferably the fibers forming the fiber structure have a mean diameter of no greater than 10 μm and contain substantially no fibers with fiber lengths of less than 20 μm.

Any process that yields the aforementioned fibers may be employed for production of a fiber structure of the invention, but there may be mentioned as a preferred mode of the production process one including a stage wherein a condensate with at least 80 mol% L-lactic acid based on the total repeating units and a condensate with at least 80 mol% D-lactic acid based on the total repeating units are

combined in a weight ratio of (6:4)-(4:6) and then dissolved in a solvent to produce a solution, a stage wherein the solution is spun by an electrospinning method, and a stage wherein fibers are accumulated on a collecting plate by the spinning.

There may also be mentioned as a preferred mode of the invention a production process including a stage wherein a condensate with at least 80 mol% L-lactic acid based on the total repeating units is dissolved in a solvent to produce a solution, a stage wherein a condensate with at least 80 mol% D-lactic acid based on the total repeating units is dissolved in a solvent to produce a solution, a stage in which the two solutions are mixed in a weight ratio of (6:4)-(4:6), a stage wherein the mixed solution is spun by an electrospinning method, and a stage wherein fibers are accumulated on a collecting plate by the spinning.

An electrospinning method is a method in which a solution of a fiber-forming compound is discharged into an electrostatic field formed between two electrodes, the solution is drawn toward the electrodes, and the resulting filamentous substance is accumulated on a collecting plate to obtain a fiber structure, where the filamentous substance need not be free of the solvent used to dissolve the fiber-forming compound but may also include the solvent.

For production of fibers comprising a stereo complex of poly(L-lactic acid) and poly(D-lactic acid), either melt spinning is carried out after melt kneading, or dry spinning is carried out from a solution containing the L-lactic acid condensate and poly(D-lactic acid) condensate, but in either case it has not been hitherto possible to

completely eliminate a melting point of below 190°C. However, it was found surprisingly that fibers obtained by electrospinning have essentially no melting point below 190°C.

An apparatus used in electrospinning for the production process of the invention will now be described.

The aforementioned electrodes may be of any type such as metal, inorganic or organic substances so long as they exhibit electrical conductivity, and they may also have electrical conductive thin-films of metal, inorganic or organic substances on insulators.

The electrostatic field may be formed by a pair of or more electrodes, and a high voltage may be applied to any of the electrodes. This also includes cases of using, for example, a total of three electrodes where two are high-voltage electrodes with different voltage values (for example, 15 kV and 10 kV) and one is a grounded electrode, as well as cases of using more than three electrodes.

The steps in a procedure of producing fibers for a fiber structure of the invention by electrospinning will now be explained in order.

First, a solution containing the aforementioned polylactic acid components dissolved in a solvent is prepared, where the concentration of the polylactic acid components in the solution is preferably 1-30 wt%. A low concentration of less than 1 wt% is not preferred because it will be difficult to form a fiber structure. The concentration is also preferably not greater than 30 wt% because the mean diameter of the obtained fibers will be increased. The preferred concentration range is 2-25 wt%.

The solvent used to dissolve the polylactic acid

components is not particularly restricted so long as it is capable of dissolving the polylactic acid components and evaporating off during the spinning stage of the electrospinning to form fibers.

Using a volatile solvent as the solvent is preferred as it will facilitate formation of the aforementioned depressions on the fiber surfaces. A volatile solvent according to the invention is a substance which has a boiling point of no higher than 200°C at atmospheric pressure and is a liquid at room temperature (for example, 27°C). As examples of specific volatile solvents there may be mentioned methylene chloride, chloroform, dichloroethane, tetrachloroethane, trichloroethane, dibromomethane, bromoform, tetrahydrofuran, 1,4-dioxane, 1,1,1,3,3,3-hexafluoroisopropanol, toluene, xylene and dimethylformamide, among which methylene chloride, chloroform, dichloroethane, tetrachloroethane, trichloroethane, dibromomethane, bromoform, tetrahydrofuran and 1,4-dioxane are preferred and methylene chloride is most preferred.

These solvents may be used alone, or a plurality of solvents may be combined for use as a mixed solvent.

The stage of spinning the aforementioned solution by electrospinning will now be explained. Any desired method may be employed for discharge of the solution into the electrostatic field, and for example, the solution may be supplied to a nozzle for appropriate positioning of the solution in the electrostatic field, and the solution drawn from the nozzle by the electrical field for formation into a filament.

A preferred mode of production of a fiber structure of

the invention will now be explained in greater detail with reference to Fig. 1.

An injection needle-shaped solution ejection nozzle (1 in Fig. 1) having a voltage applied by appropriate means such as a high-voltage generator (6 in Fig. 1) is fitted at the tip of the cylindrical solution-holder of a syringe (3 in Fig. 1), and the solution (2 in Fig. 1) is guided to the tip of the solution ejection nozzle. The tip of the solution ejection nozzle (1 in Fig. 1) is situated at an appropriate distance from a grounded filamentous substance-collecting electrode (5 in Fig. 1), and the solution (2 in Fig. 1) is ejected from the tip of the solution ejection nozzle (1 in Fig. 1) to form a filamentous substance between the nozzle tip solution and the filamentous substance-collecting electrode (5 in Fig. 1).

As a different mode, shown in Fig. 2, fine droplets of the solution (not shown) may be introduced into an electrostatic field, with the only condition being that the solution (2 in Fig. 2) is placed in the electrostatic field and held at a distance from the filamentous substance-collecting electrode (5 in Fig. 2) which allows formation into a filament. For example, an electrode (4 in Fig. 2) counter to the filamentous substance-collecting electrode may be inserted directly into the solution (2 in Fig. 2) in the holder (3 in Fig. 2) with the solution ejection nozzle (1 in Fig. 2).

When the solution is ejected through the nozzle into the electrostatic field, the filamentous substance production speed can be increased by using a plurality of nozzles in parallel. Also, the distance between electrodes will depend on the charge, nozzle dimensions, ejection

volume of the solution from the nozzle and the solution concentration, but a distance of 5-20 cm has been found to be suitable for approximately 10 kV. The applied electrostatic potential will normally be 3-100 kV, preferably 5-50 kV and more preferably 5-30 kV. The desired potential can be produced by any appropriate method known in the prior art.

The two modes described above employ an electrode as the collecting plate, but a material serving as the collecting plate may also be placed between the electrodes, to provide a collecting plate separate from the electrodes for collection of a filament laminate. In this case, a belt-like substance, for example, is placed between the electrodes and used as the collecting plate to allow continuous production.

The stage of obtaining a fiber structure accumulated on the collecting plate will now be explained. According to the invention, a filamentous substance is formed by evaporation of the solvent, depending on the conditions, while the solution is drawn toward the collecting plate. Although the solvent will usually evaporate completely during the period of collection on the collecting plate at room temperature, the drawing may be accomplished under reduced pressure conditions if the solvent evaporation is insufficient. A fiber structure satisfying at least the fiber mean diameter and fiber length is formed upon collection on the collecting plate. The temperature for drawing may be adjusted according to the evaporation behavior of the solvent and the viscosity of the spinning solution, and will normally be in the range of 0-100°C.

A relative humidity of 20-80% RH is preferred between

the nozzle and collecting plate where the filamentous substance is formed. If the relative humidity is outside of this range, it will be difficult to accomplish stable spinning for prolonged periods. A more preferred relative humidity range is 30-70% RH.

The fiber structure obtained by the production process of the invention may be used alone, but it may also be used in combination with other structural members depending on handleability and other essential factors. For example, a nonwoven fabric, woven fabric or film that can serve as a support material may be used as the collecting plate and the filament laminate formed thereover to allow fabrication of a member comprising a combination of the support material and the filament laminate.

The obtained fiber structure may also be subjected to heat treatment or chemical treatment, and the polylactic acid may be mixed with an emulsion or an organic or inorganic powder or filler at any stage prior to spinning.

For example, any of various catalysts may be supported on the fiber structure of the invention for use as a catalyst-supporting base material.

Examples

The present invention will now be explained by examples, with the understanding that the invention is not limited to these examples. The evaluations of properties in the examples and comparative examples were carried out by the following methods.

Fiber mean diameter:

The fiber diameter was measured by selecting 20 random

locations from a photograph taken of the surface of the obtained fiber structure (2000 magnification) using a scanning electron microscope (S-2400 by Hitachi, Ltd.), and the average value of the fiber diameters (n=20) was determined and recorded as the fiber mean diameter.

Presence of fibers with fiber lengths of less than 20 μm:

A photograph taken of the surface of the obtained fiber structure (2000 magnification) using a scanning electron microscope (S-2400 by Hitachi, Ltd.) was observed to confirm the presence of fibers with fiber lengths of less than 20 μm.

Depressions in fiber surface structure:

An scanning electron microscope photograph (8000 magnification) was taken of the surface of the obtained fiber structure. General purpose image processing software (NanoHunter NS2K-Pro/Lt Ver. 5.2 by Nano System Corp.) was used to select the most clearly imaged fiber in the photograph, and after establishing an imaginary line A running through the center axis of the selected fiber and imaginary lines B and B' along both outer edges of the selected fiber, two imaginary lines C and C' running between the centers between the imaginary line A and imaginary lines B, B' were established.

The section defined by the established imaginary lines C, C' and the edges of the photograph was extracted with the image processing software, and the area percentage of depressions in the region was determined.

The area percentage was measured for each of 10 arbitrary locations of the fiber structure in the electron

microscope photograph, and the average was determined.

Weight-average molecular weight:

The weight-average molecular weight was measured with a GPC-11 by Showa Denko K.K. (Column: SHODEX LF-804, solvent: chloroform, detector: RI, styrene equivalent).

Melting point:

A DSC curve for the obtained fiber structure was measured using a differential scanning calorimeter (DSC TA-2920 by Texas Instruments), and the melting point was determined from the isothermal peak.

Example 1

After mixing 500 ppm of tin octylate with D-lactide, polymerization was conducted in a stirrer-equipped reactor at 200°C for 60 minutes under a nitrogen atmosphere, to obtain a poly(D-lactic acid) homopolymer with a weight-average molecular weight of 120,000.

There were prepared a solution of 1 part by weight of the obtained poly(D-lactic acid) in 9 parts by weight of methylene chloride and a solution of 1 part by weight of poly(L-lactic acid) (Lacty 9031™ by Shimadzu Corp., weight-average molecular weight: 168,000) in 9 parts by weight of methylene chloride, and both solutions were mixed at 5 parts by weight each.

Next, the apparatus shown in Fig. 2 was used for discharge of the solution for 5 minutes onto a filamentous substance-collecting electrode 5. The inner diameter of the ejection nozzle (1 in Fig. 2) was 0.8 mm, the voltage was 12 kV, the distance from the ejection nozzle (1 in Fig. 2) to the filamentous substance-collecting electrode (5 in

Fig. 2) was 12 cm and the relative humidity was 35% RH. Upon observing the obtained fiber structure with a scanning electron microscope (S-2400 by Hitachi, Ltd.), the mean fiber diameter was 3 μm and no fibers were present with fiber lengths of less than 20 μm. The mean diameter of the depressions on the fiber surfaces was 0.2 μm, and the percentage of the fiber surface area occupied by the depressions was 23%. Scanning electron microscope photographs of the fiber structure are shown in Figs. 3 and 4.

As a result of DSC measurement of the obtained fiber structure, the melting point was 216°C and no endothermic peak was observed below 190°C.

Example 2

There were mixed 6 parts by weight of a solution of 1 part by weight of the poly(D-lactic acid) in 9 parts by weight of methylene chloride and 4 parts by weight of a solution of 1 part by weight of poly(L-lactic acid) in 9 parts by weight of methylene chloride, and a fiber structure was obtained in the same manner as Example 1, except that the distance from the ejection nozzle to the filamentous substance-collecting electrode was 10 cm.

The mean fiber diameter of the obtained fiber structure was 4 μm, and no fibers were present with fiber lengths of less than 20 μm. The mean diameter of the depressions on the fiber surfaces was 0.2 μm, and the percentage of the fiber surface area occupied by the depressions was 22%. Scanning electron microscope photographs of the fiber structure are shown in Figs. 5 and 6.

As a result of DSC measurement of the obtained fiber

structure, the melting point was 218°C and no endothermic peak was observed below 190°C.

Comparative Example 1

A fiber structure was obtained in the same manner as Example 2, except for mixing 7 parts by weight of a solution of 1 part by weight of the poly(D-lactic acid) in 9 parts by weight of methylene chloride and 3 parts by weight of a solution of 1 part by weight of poly(L-lactic acid) in 9 parts by weight of methylene chloride.

The mean fiber diameter of the obtained fiber structure was 3 μm, and no fibers were present with fiber lengths of less than 20 μm. The mean diameter of the depressions on the fiber surfaces was 0.2 μm, and the percentage of the fiber surface area occupied by the depressions was 31%. Scanning electron microscope photographs of the fiber structure are shown in Figs. 7 and 8.

As a result of DSC measurement of the obtained fiber structure, the main melting point was 219°C and a small endothermic peak was observed at 165°C.

Comparative Example 2

A fiber structure was obtained in the same manner as Example 2, except that only a solution of 1 part by weight of poly(D-lactic acid) in 9 parts by weight of methylene chloride was used.

The mean fiber diameter of the obtained fiber structure was 2 μm, and no fibers were present with fiber lengths of less than 20 μm. The mean diameter of the depressions on the fiber surfaces was 0.2 μm, and the percentage of the fiber surface area occupied by the depressions was 21%. Scanning electron microscope

photographs of the fiber structure are shown in Figs. 9 and 10.

As a result of DSC measurement of the obtained fiber structure, the melting point was 174°C.

Comparative Example 3

A fiber structure was obtained in the same manner as Example 2, except that only a solution of 0.7 part by weight of poly(L-lactic acid) in 9.3 parts by weight of methylene chloride was used.

The mean fiber diameter of the obtained fiber structure was 3 μm, and no fibers were present with fiber lengths of less than 20 μm. The mean diameter of the depressions on the fiber surfaces was 0.2 μm, and the percentage of the fiber surface area occupied by the depressions was 27%. Scanning electron microscope photographs of the fiber structure are shown in Figs. 11 and 12.

As a result of DSC measurement of the obtained fiber structure, the melting point was 172°C.

Example 3

A fiber structure was obtained in the same manner as Example 2, except that a methylene chloride/DMF mixed solvent (weight ratio: 8/2) was used instead of methylene chloride. The mean fiber diameter of the obtained fiber structure was 2 μm, and no fibers were present with fiber lengths of less than 20 μm. No fiber surface depressions were observed. Scanning electron microscope photographs of the fiber structure are shown in Figs. 13 and 14.

As a result of DSC measurement of the obtained fiber structure, the melting point was 220°C and no endothermic peak was observed below 190°C.

Example 4

A fiber structure was obtained in the same manner as Example 2, except for mixing 4 parts by weight of a solution of 1 part by weight of poly(D-lactic acid) in 9 parts by weight of a methylene chloride/DMF mixed solvent (weight ratio: 8/2) and 6 parts by weight of a solution of 1 part by weight of poly(L-lactic acid) in 9 parts by weight of a methylene chloride/DMF mixed solvent (weight ratio: 8/2).

The mean fiber diameter of the obtained fiber structure was 2 μm, and no fibers were present with fiber lengths of less than 20 μm. No fiber surface depressions were observed. Scanning electron microscope photographs of the fiber structure are shown in Figs. 15 and 16.

As a result of DSC measurement of the obtained fiber structure, the melting point was 221°C and no endothermic peak was observed below 190°C.

Comparative Example 4

A fiber structure was obtained in the same manner as Example 2, except for mixing 3 parts by weight of a solution of 1 part by weight of poly(D-lactic acid) in 9 parts by weight of a methylene chloride/DMF mixed solvent (weight ratio: 8/2) and 7 parts by weight of a solution of 1 part by weight of poly(L-lactic acid) in 9 parts by weight of a methylene chloride/DMF mixed solvent (weight ratio: 8/2).

The mean fiber diameter of the obtained fiber structure was 2 μm, and no fibers were present with fiber lengths of less than 20 μm. No fiber surface depressions were observed. Scanning electron microscope photographs of the fiber structure are shown in Figs. 17 and 18.

As a result of DSC measurement of the obtained fiber structure, the main melting point was 221°C and a small endothermic peak was observed at 156°C.

Comparative Example 5

A fiber structure was obtained in the same manner as Example 2, except that only a solution of 1 part by weight poly(D-lactic acid) in 9 parts by weight of a methylene chloride/DMF mixed solvent (weight ratio: 8/2) was used.

The mean fiber diameter of the obtained fiber structure was 1 μm, and no fibers were present with fiber lengths of less than 20 μm. No fiber surface depressions were observed. Scanning electron microscope photographs of the fiber structure are shown in Figs. 19 and 20.

As a result of DSC measurement of the obtained fiber structure, the melting point was 172°C.

Comparative Example 6

A fiber structure was obtained in the same manner as Example 2, except that only a solution of 1 part by weight poly(L-lactic acid) in 9 parts by weight of a methylene chloride/DMF mixed solvent (weight ratio: 8/2) was used.

The mean fiber diameter of the obtained fiber structure was 3 μm, and no fibers were present with fiber lengths of less than 20 μm. Some corrugation of the fiber surfaces was seen, but no depressions were observed. Scanning electron microscope photographs of the fiber structure are shown in Figs. 21 and 22.

As a result of DSC measurement of the obtained fiber structure, the melting point was 170°C.

CLAIMS

1. Ultrafine polylactic acid fibers comprising as the main constituent component a polylactic acid component with a melting point of 190°C or higher, with a mean fiber diameter of no greater than 10 μm and fiber lengths of 20 μm or greater, and containing substantially no constituent component with a melting point of below 190°C.

2. (deleted)

3. Fibers according to claim 1, having depressions with diameters of 0.01-1 μm on the fiber surfaces, the depressions constituting 10-95% of the fiber surfaces.

4. Fibers according to claim 1, wherein the polylactic acid component is a blend of a condensate with at least 80 mol% L-lactic acid based on the total repeating units and a condensate with at least 80 mol% D-lactic acid based on the total repeating units.

5. Fibers according to claim 4, wherein the weight ratio of the L-lactic acid condensate and the D-lactic acid condensate is (6:4)-(4:6).

6. A fiber structure comprising at least ultrafine polylactic acid fibers according to claim 1.

7. A fiber structure according to claim 6, wherein the fibers forming the fiber structure have a mean diameter of no greater than 10 μm and contain substantially no fibers with fiber lengths of less than 20 μm.

8. A production process for a fiber structure, which includes a stage wherein a condensate with at least 80 mol% L-lactic acid based on the total repeating units and a condensate with at least 80 mol% D-lactic acid based on the

total repeating units are combined in a weight ratio of (6:4)-(4:6) and then dissolved in a solvent to produce a solution, a stage wherein said solution is spun by an electrospinning method, and a stage wherein a fiber structure is accumulated on a collecting plate by said spinning.

9. A production process according to claim 8, wherein the solvent is a volatile solvent.

10. A production process according to claim 8, wherein the relative humidity is in the range of 20-80% RH between the nozzle and collecting plate where the filamentous substance is formed in the stage of spinning by electrospinning.

11. A production process for a fiber structure which includes a stage wherein a condensate with at least 80 mol% L-lactic acid based on the total repeating units is dissolved in a solvent to produce a solution, a stage wherein a condensate with at least 80 mol% D-lactic acid based on the total repeating units is dissolved in a solvent to produce a solution, a stage in which the two solutions are mixed in a weight ratio of (6:4)-(4:6), a stage wherein said mixed solution is spun by an electrospinning method, and a stage wherein a fiber structure is accumulated on a collecting board by said spinning.

12. A production process according to claim 11, wherein the solvent is a volatile solvent.

13. A production process according to claim 12, wherein the volatile solvent is at least one selected from the group consisting of methylene chloride, chloroform, dichloroethane, tetrachloroethane, trichloroethane,

dibromomethane, bromoform, tetrahydrofuran and 1,4-dioxane.

14. A production process according to claim 11, wherein the relative humidity is in the range of 20-80% RH between the nozzle and collecting plate where the filamentous substance is formed in the stage of spinning by electrospinning.

Application number/numéro de demande: JP05-04165

Figures:

Pages: 3 to 22

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Unscannable items
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Documents reçus avec cette demande ne pouvant être balayés
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Fig. 1

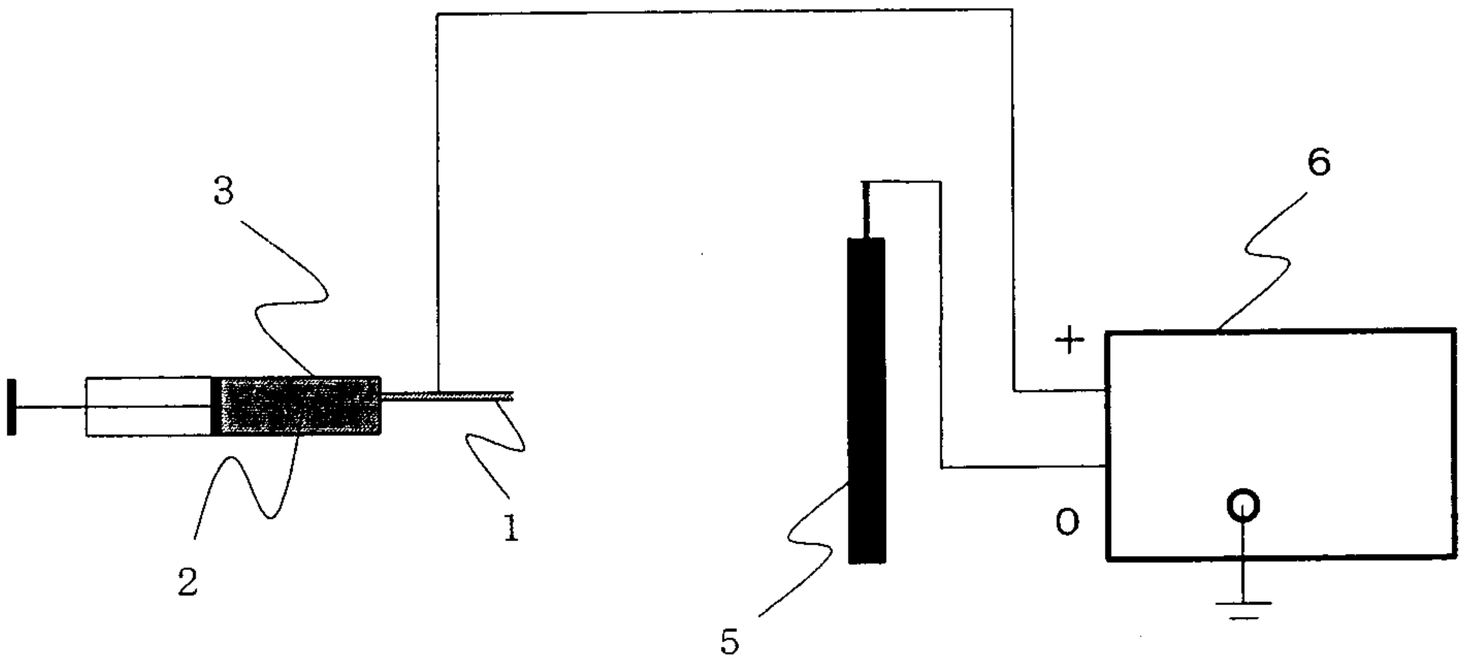
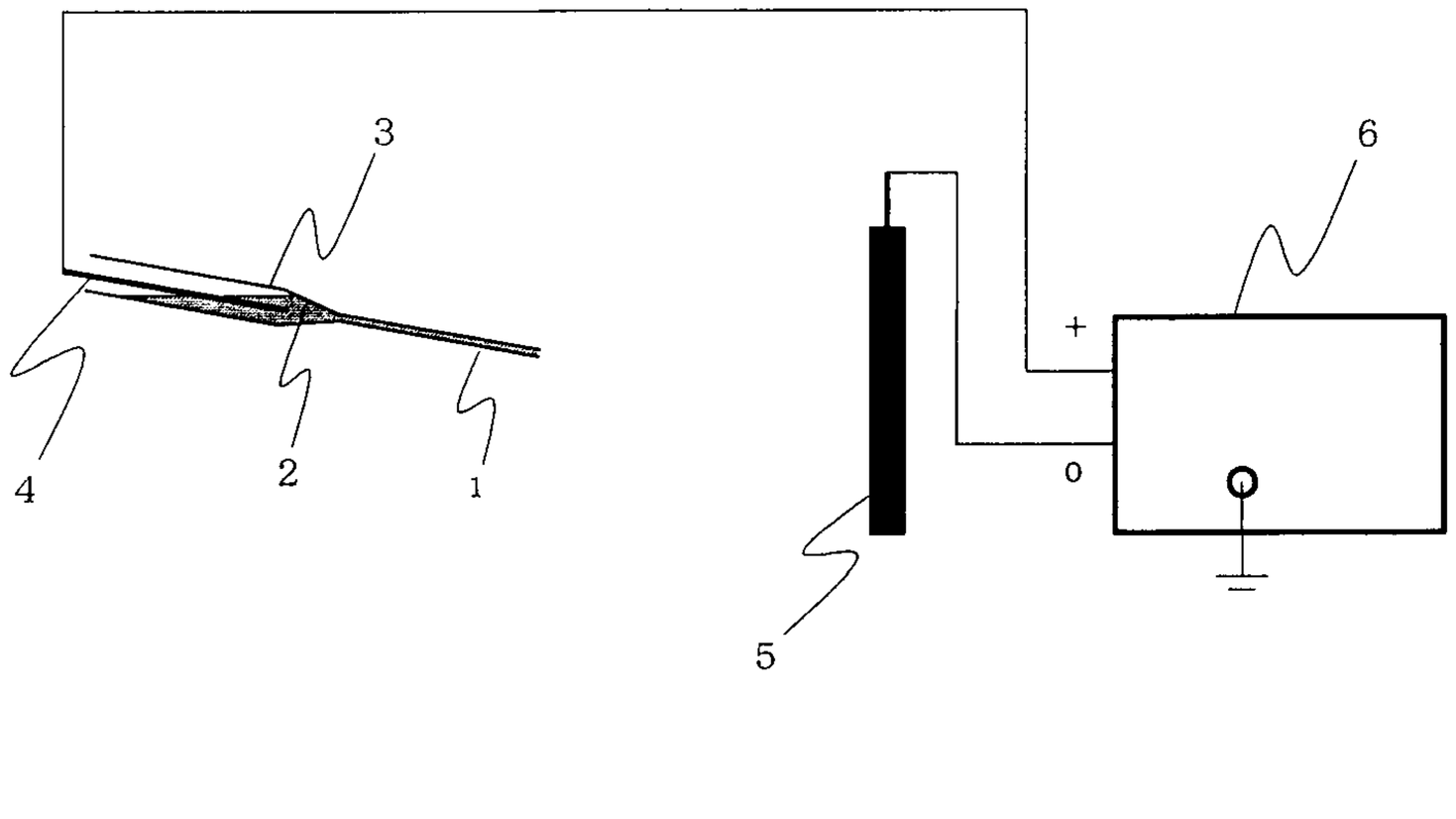
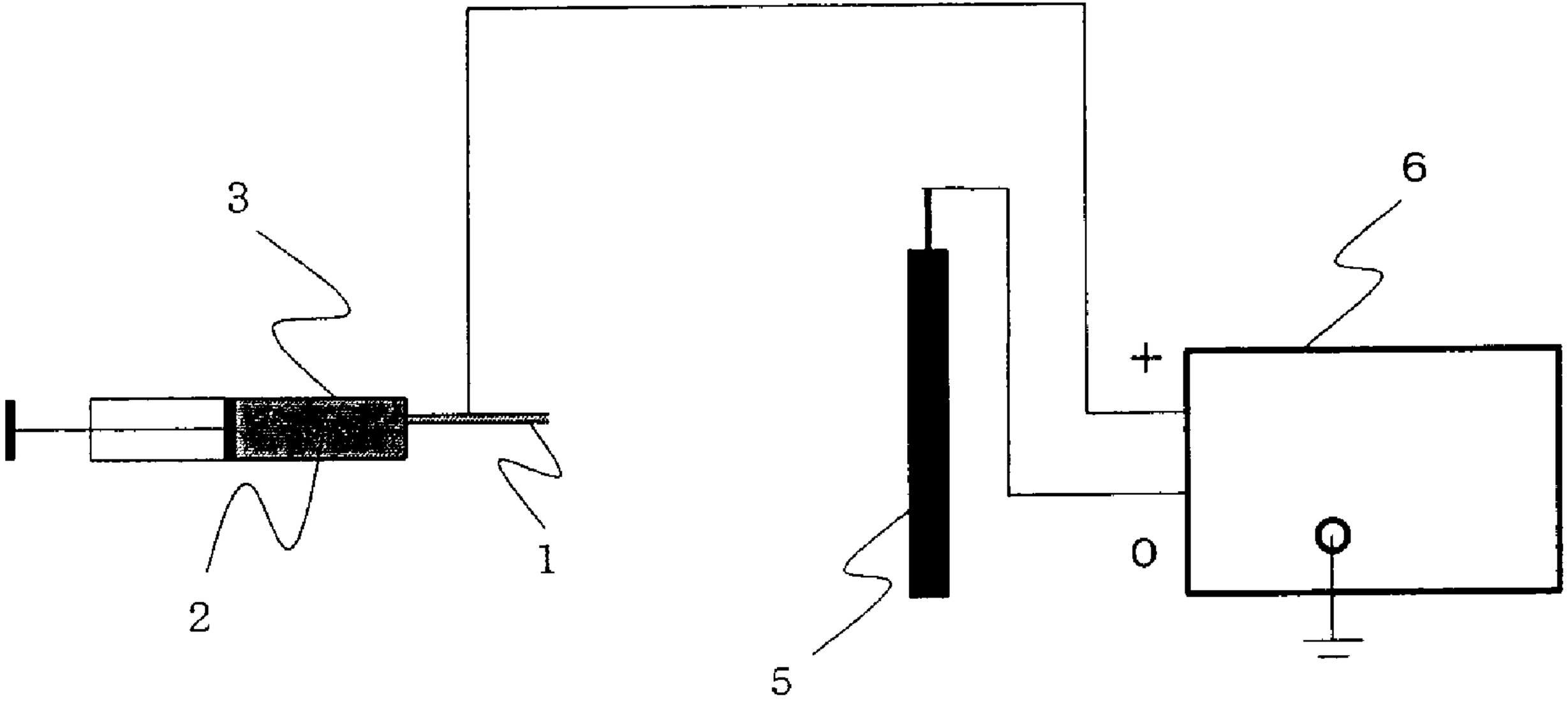


Fig. 2

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