(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 438 598 A1**

(12) EUROPEAN PATENT APPLICATION published in accordance with Art. 158(3) EPC

(21) Application number: **90910940.7**

(22) Date of filing: **11.07.90**

(86) International application number:
PCT/JP90/00890

(87) International publication number:
WO 91/00935 (24.01.91 91/03)

(51) Int. Cl.5: **D01F 6/46**, D01F 6/04,
D01F 6/30

(30) Priority: **13.07.89 JP 181557/89**

(43) Date of publication of application:
31.07.91 Bulletin 91/31

(84) Designated Contracting States:
DE FR GB IT

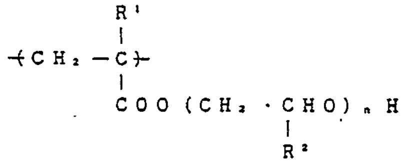
(71) Applicant: **MITSUBISHI RAYON CO., LTD.**
3-19, Kyobashi 2-chome Chuo-Ku
Tokyo 104(JP)

(72) Inventor: **KOSHOJI, Toshinobu Mitsubishi Rayon Co., Ltd.**
1-2, Ushikawadori 4-chome
Toyohashi-shi Aichi 440(JP)
Inventor: **HONDA, Hironari Mitsubishi Rayon Co., Ltd.**
1-2, Ushikawadori 4-chome
Toyoahashi-shi Aichi 440(JP)
Inventor: **OKAMURA, Kiyonobu Mitsubishi Rayon Co., Ltd.**
1-2, Ushikawadori 4-chome
Toyohashi-shi Aichi 440(JP)
Inventor: **MISOO, Kunio Mitsubishi Rayon Co., Ltd.**
1-2, Ushikawadori 4-chome
Toyohashi-shi Aichi 440(JP)

(74) Representative: **Hansen, Bernd, Dr. Dipl.-Chem. et al**
Hoffmann, Eitle & Partner Patent- und Rechtsanwälte Arabellastrasse 4
W-8000 München 81(DE)

(54) POROUS FIBER AND PRODUCTION THEREOF.

(57) A porous fiber having a pore structure comprising interconnected spaces enclosed with lamellae and a number of longitudinally arranged fibrils that connect the lamellae with each other all over the fiber, which is produced by blending a polyolefin with a hydrophilic copolymer mainly comprising monomer units represented by formula (I) and ethylene units, melt spinning the blend, and stretching the resulting fiber; wherein R^1 and R^2 represent each independently hydrogen or methyl, and n is 1 to 9. The obtained fiber has permanent hydrophilicity and a large surface area, is very lightweight and soft to the touch, has a fair white color without transparence, and is endowed with excellent mechanical properties in spite of its high void fraction.



$$-\!\left(CH_2-\overset{\displaystyle R^1}{\underset{\displaystyle COO(CH_2\cdot\underset{\displaystyle R^2}{CH}O)_nH}{C}}\right)\!- \quad (I)$$

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TECHNICAL FIELD

This invention relates to porous polyolefin fibers.

Background Art

Recently, the use of fibers for clothing and for industrial materials has progressively been diversified and therefore, as a part of the diversification, there are increasing demands for fibers which are light in weight and have an appropriate strength as well as a soft hand feeling.

There is an method to achive lighter weight and soft hand feeling by making the fibers porous.

To make fibers porous, there have been used, for example, a method comprising blending a foaming agent with a thermoplastic polymer and melt-spinning the resulting blend to decompose the foaming agent in the stage of spinning so that the spun fiber is allowed to foam to make it porous, a method comprising spinning a blend of a thermoplastic polymer with an extractable pore-forming additive (inorganic salts, organic low molecular compounds, etc.) and extracting the additive with a suitable solvent to make the fiber porous, etc.

However, in the method in which a foaming agent is blended, it is difficult to obtain uniform and minute porous structures and therefore to obtain porous fibers of stable quality. In other words, an intention of increasing the porosity may cause frequent occurrence of yarn breakage and significant reduction in strength. As a result, it is difficult to obtain fibers with high porosity, and the process stability in the spinning step is also low.

In the extraction method, the processes are complicated. Further, it is difficult to completely remove the additive from the fibers by extraction and the additive tends to remain in the fiber products as impurity, which affect their hand feeling so seriously that it is difficult to obtain the fibers of fairly good hand feeling. Moreover, increased porosity may cause significant reduction of the strength. The extraction method involves these problems so that it is also not fully satisfactory at present.

On the other hand, as one mode of the diversification, fibers excellent in water absorbing capacity and sweat absorbing capacity have also been demanded strongly and hence the development of fibers superb in these properties is also being made actively.

These properties may be obtained by using fibers imparted with hydrophilicity.

A variety of materials are being available for use as hydrophilic fibers, but attentions are being paid to the development of polyolefin fibers, which are excellent in strength, etc., to the uses which need hydrophilicity.

Since polyolefins are hydrophobic materials, it is necessary to hydrophilize them in order to develop polyolefin fibers to the uses which need hydrophilicity. However, in the hydrophilizing method using hydrophilizing agents such as surface active agents, the resulting hydrophilic fibers are liable to lose hydrophilicity due to the elimination of the hydrophilizing agents upon comming into contact with water. Further, even if polyolefins blended with hydrophilic substances in common use are melt-spun, it is not possible to obtain fibers of good properties owing to the poor affinity of the hydrophilic substances to the polyolefins.

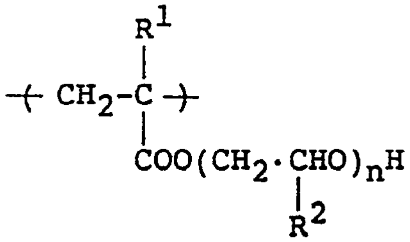
Disclosure of the Invention

The present inventors have made intensive investigations in view of the above-described state of art and finally found that by melt-spinning a blend of a polyolefin with a hydrophilic copolymer having specific properties and stretching the resulting fiber, it becomes possible to obtain a porous fiber, which has an excellent porous structure and permanent hydrcphilicity and is capable of satisfying simultaneously such properties as lightness in weight, soft hand feeling and water absorbing capacity, leading to completion of the present invention.

An object of the present invention is to provide porous fibers which are substantially hydrophilic, are very light in weight, have soft hand feeling, and exhibit superb mechanical characteristics in spite of high porosity.

Another object of the present invention is to provide porous fibers which do not involve the problems of residual solvents or pore-making additives occurring in the porous fibers produced by the extraction method.

The porous fiber of the present invention capable of attaining these objects comprises a hydrophilic copolymer X, composed principally of monomer units A represented by the following formula:



$$-\!\!\left(\,CH_2-\overset{\displaystyle R^1}{\underset{\displaystyle COO(CH_2\cdot\underset{\displaystyle R^2}{CHO})_nH}{C}}\,\right)\!\!-$$

wherein R^1 and R^2 independently represent hydrogen or methyl and n is a number in the range of 1 to 9 and ethylene units B, and a polyolefin Y, and has a porous structure in which intercommunicating pores are formed by lamellae and a large number of longitudinally oriented fibrils interconnecting said lamellae.

The porous fiber can be prepared by the process comprising the step of melt-spinning a blend of a hydrophilic copolymer X, composed principally of monomer units A represented by the foregoing fomula and ethylene units B, and a polyolefin Y to obtain an unstretched fiber and the step of heat-treating said unstretched fiber in a vacuum or an inert gas medium at a temperature not higher than the melting point of the polyolefin Y for a period of one hour or more and stretching the resulting fiber to make it porous.

The porous polyolefin fibers of the present invention have porous structures in which intercommunicating pores are formed by lamellae and a large number of longitudinally oriented fibrils interconnecting said lamellae in the whole sections from the surfaces to the centers of the fibers. In consequence, the fibers have large surface areas, are very light in weight, have soft hand feeling, are of beautiful white with no transparence and, in addition, exhibit excellent mechanical characteristics in spite of high porosity.

As described above, the porous fibers obtained by the extraction method often contain residual solvents used for extraction or residual additives used for pore-making. On the other hand, since the porous fibers of the present invention are made porous by stretching unstretched fibers obtained by melt-spinning blends of specific compositions, they do not contain any solvents or pore-making additives, as is the case with the porous fibers derived from the extraction method. Accordingly, the porous fibers of the present invention are sanitary materials and besides have permanent hydrophilicity, so that they are best suited for materials for clothing such as underwears, which directly come in contact with the skin and hence call for good sweat absorbing capacity, or for materials for medical cloth.

Further, making use of the large moisture content and the water absorbing capacity in the pores, the porous fibers of the present invention may be employed as materials for various industrial uses, including wipers, adsorptive materials, etc.

Best Mode for Carrying out the Invention

The porous fiber of the present invention comprises a hydrophilic copolymer X, composed mainly of monomer units A represented by the foregoing formula and ethylene units B, and a polyolefin Y, and has a porous structure in which intercommunicating pores are formed by lamellae and a large number of longitudinally oriented fibrils interconnecting said lamellae.

The polyolefins Y used as one component of the porous fibers of the present invention may include, for example, polyethylene, polypropylene, poly-3-methylbutene-1, poly-4-methylpentene-1, etc.

The polyolefins Y which have a high degree of crystallinity may preferably be used. Therefore, it is preferable to select such polymers that the unstretched fiber obtained by melt-spinning a blend of each of the polymers with the hydrophylic copolymer X described below have a degree of crystallinity of 40% or more, preferably 50% or more and a degree of crystal orientation of 50% or more, preferably 60% or more.

The value of n in the above-described formula representing a unit A signifies the average polymerization degree of the alkylene glycol units in the unit A (i.e., the average number of oxyalkylene groups), which may be in the range of 1 to 9.

If n is greater than 9, polyalkylene glycol (meth) acrylate used as a component for the introduction of units A becomes so viscous that it is difficult to react it uniformly with ethylene used as a component for the introduction of units B, and hence no hydrophilic copolymers X can be obtained.

Where n ranges from 1 to 2, high reactivity can be achieved in the reaction between the component for the introduction of units A and the component for the introduction of units B, making it possible to industrially produce a hydrophilic copolymer X showing little variation in quality. Thus, there can be obtained hydrophilic porous fibers containing little water-soluble matter.

In a hydrophilic copolymer X, various units A differing in the polymerization degree of the alkylene glycol units and in the type of R^1 and R^2 may be present in admixture. For example, oxyethylene blocks and oxypropylene blocks may be present in admixture.

In the hydrophilic copolymer X, no particular limitation is placed on the ratio between units A and B. However, the content of units A is preferably in the range of 80 to 10% by weight (units A/units B = 80/20 to 10/90, by weight), for reasons given below. Specifically, if the content of units A is less than 10% by weight, the resulting porous fiber does not show sufficient hydrophilicity. On the other hand, if the content of units A is greater than 80% by weight, the hydrophilic copolymer X itself generally contains large amounts of very-low-molecular-weight components and, therefore, tends to dissolve out from the porous fiber formed of a blend of this copolymer and a polyolefin Y.

In order to allow the porous fiber to exhibit sufficient hydrophilicity, the content of units A is more preferably in the range of 70 to 15% by weight and most preferably in the range of 70 to 40% by weight.

No particular limitation is imposed on the molecular weight of a hydrophilic copolymer X. However, in order to obtain a porous fiber exhibiting permanent hydrophilicity, the hydrophilic copolymer X preferably has a relatively high molecular weight. More specifically, it preferably has an intrinsic viscosity $[\eta]$ of about 0.07 to 0.40 dl/g as measured in xylene at 75° C. If the value of $[\eta]$ is below the lower limit of this range, the hydrophilic copolymer tends to bleed out during use. On the other hand, if the value of $[\eta]$ is above the upper limit of the aforesaid range, the fluidity of the hydrophilic copolymer is so low that the resultant porous fiber tends to have lower proportions of the hydrophilic copolymer in the surface of the porous fiber, inclusive of the pore surface thereof.

A hydrophilic copolymer X basically comprises units A and units B. However, a hydrophilic copolymer X may contain a third type of units in addition to units A and B, provided that they are present in such an amount as not to impair the hydrophilicity or like properties of the resulting porous fiber.

Examples of the third type of units include ethylenically unsaturated monomer units C derived from an ethylenically unsaturated carboxylic acid ester, an ethylenically unsaturated vinyl ester or an ethylenically unsaturated carboxylic acid. Units C may be present in an amount of about 1 to 40 parts by weight, preferably about 1 to 10 parts by weight, per 100 parts by weight of units A and B.

In the porous fibers of the present invention, no particular limitation is placed on the proportion of the hydrophilic copolymer X to the polyolefin Y. It may be determined at will depending on the degree of hydrophilicity required and easiness of production. It is generally possible to determine the proportion of X to Y in accordance with the contents of units A and B in the hydrophilic copolymer. As a rule, when the content of units A in a hydrophilic copolymer X is high, the resulting porous fiber exhibits sufficient hydrophilicity even if the content of X in the porous fiber is low. However, when the content of units A is low, the content of X in the porous fiber must be increased in order that the porous fiber can exhibit sufficient hydrophilicity.

Where a melt spinning/stretching process is employed to produce the porous fibers, the amounts of X and Y blended can be determined in consideration of the fact that, if a hydrophilic copolymer X has a high content of units A, the growth of lamellar crystals in the spun unstretched fiber is inhibited by using a large amount of the hydrophilic copolymer X in the starting polymer blend, whereas if a hydrophilic copolymer X has a low content of units A, the growth of lamellar crystals in the unstretched fiber is scarcely inhibited even by using a large amount of X in the starting polymer blend.

In the porous fibers of the present invention, the content of a polyolefin Y is preferably in the range of about 95 to 50% by weight (X/Y = 5/95 to 50/50, by weight). If the content of a polyolefin is less than the lower limit of this range, it becomes difficult to grow lamellar crystals fully in the unstretched fiber. Thus, it becomes difficult to obtain a fiber having an excellent porous structure.

The porous fibers of the present invention may preferably have a porosity of 30 to 80%, a tensile strength of 0.5 to 8 g/d, and a elongation of 1 to 300%. If the porosity is below the lower limit of the above range, the porous fiber is apt to be insufficient in lightness and hand feeling proportionately, while when it exceeds the upper limit, its strength tends to be inadquate. In consideration of the uses for clothing, it is preferable that the strength and elongation are in the aforesaid respective ranges.

The process for the production of the porous fibers according to the present invention will be illustrated hereunder.

First, the above-described hydrophilic copolymer X and polyolefin Y are blended in a sufficiently intimate manner. Useful blending methods include the method in which the polymers are blended by means of a suitable blender such as V-type blender, and the method in which the polymers are melt-blended in a melt extruder and then pelletized.

The polymer blend is then melt-spun by means of an ordinary spinning machine and wound as an unstretched fiber. The spinning temperature may preferably be higher than the melting point of the polyolefin Y (hereinafter referred to as Tm) by 20° C or more and does not exceed (Tm + 80° C). When the spinning is effected at a lower temperature than the lower limit of this temperature range, the resulting unstretched fiber will be highly oriented, but the maximum amount of stretching achievable in the subsequent stretching step for making it porous may not be increased, thus leading to failure in obtaining porous fibers having sufficiently high porosity. Therefore, such conditions are not preferred. On the contrary, if the spinning is carried out at temperatures above the upper limit of the aforesaid temperature range, it is difficult to obtain fibers with high porosity. Therefore, such temperatures are not preferred.

In order to perform stable spinning and to increase the degree of crystallinity of the spun unstretched fibers, it is preferable to provide a slow cooling section with a length of about 1 to 3 m and an atmosphere temperature of about 50 to 100 ° C right under the spinneret.

If the length of the slow cooling section is less than 1 m or its atmosphere temperature is lower than 50 ° C, yarn breakage often occurs right under the spinneret so that the process stability tends to be reduced. Therefore, such conditions are not preferred. On the other hand, if the length of the slow cooling section is in excess of 3 m or the atmosphere temperature is above 100 ° C, there is such a tendency that cooling of the fiber is insufficient and the substantial draft is reduced. Thus, these conditions are not preferred in view of the crystal orientation of the resulting unstretched fiber.

The spinning draft to be adopted is slightly lower than in the case of spinning a polyolefin alone. It is preferably approx. 50 to 2,000, more preferably approx. 100 to 1,000.

The unstretched fiber thus obtained is heat-treated (annealed) under constant length or relaxed conditions at a temperature lower than Tm, preferably in the range from (Tm - 10 ° C) to (Tm - 30 ° C), for a period of one hour or more in order to enhance its degree of crystallinity. Although longer treating times are more desirable, it is preferable from the economical viewpoint to employ a treating time of about 48 hours or less and more preferably in the range of about 3 to 48 hours.

If such a long-time heat-treating is performed in air, the hydrophilic copolymer X deteriorates during the heat-treatment. In the present invention, therefore, it is performed in an inert gas or a vacuum.

The heat-treated product is stretched so as to render it porous. Usually, a stretching procedure comprising a combination of cold stretching and hot stretching is employed. Specifically, the product is first cold-stretched at a temperature ranging from about (Tm - 220 ° C) to (Tm - 80 ° C), preferably from (Tm - 160 ° C) to (Tm - 90 ° C), and then hot-stretched at a temperature ranging from about (Tm - 60 ° C) to (Tm - 5 ° C).

Each of these cold-stretching and hot-stretching steps may be performed in two or more stages.

The cold stretching is an important step in the production of the fibers of the present invention. In this step, microcracks are evolved in the amorphous portions between lamellar crystals in the highly-oriented crystalline unstretched fiber, and they are spread by the thermo-plasticifying stretching in the subsequent hot stretching, whereby the above-described specific porous structure is formed. The amount of cold stretching is preferably in the range of 5 to 100%, and the amount of hot stretching is preferably so determined that the total amount of stretching achieved by both cold stretching and hot stretching is in the range of 100 to 700%. Incidentally, hot stretching at a temperature above (Tm - 5 ° C) will cause the fibers to become transparent and hence the intended porous structures will not be obtained. If the hot stretching temperature is below the above-described lower limit value, the porosity will be reduced with decreasing temperature. Therefore, such conditions are not preferred. If the total amount of stetching exceeds 700%, yarn breakage may frequently occur during the stretching operation. The porous fiber thus obtained has substantial morphological stability as a result of hot stretching. If desired, however, the porous fiber may be thermally set in one stage or more under strained (constant length) or partially relaxed conditions at a temperature ranging from (Tm - 60 ° C) to (Tm - 5 ° C) in dry or wet atmosphere. Further, the porous fiber may also be treated with hot water or steam at about 50 to 120 ° C, as required, with a view to enhancing the hydrophilicity of the fiber.

(Examples)

The present invention is further illustrated by the following examples. In these examples, the degree of crystallinity of the polymer blend was determined by integrating the diffracted light intensities in all directions with a wide-angle X-ray diffractometer and calculating the degree of crystallinity from the following equation.

Degree of crystallinity Xc = (Integrated value of all diffracted light intensities) - (Integrated value of diffracted light intensities in amorphous portions)/(Integrated value of all diffracted light intensities)

The degree of crystal orientation was determined by measuring the diffracted light intensity in the (110) plane with a wide-angle X-ray diffractometer, obtaining the half-value width of its distribution in the axial direction of the fiber, and calculating the degree of crystal orientation from the following equation.

Degree of crystal orientation (%) =
$H_{(110)}/(180 - H_{(110)}) \times 100$

[$H_{(110)}$: the half-value width in the (110) plane]

The contents of units A and B in a hydrophilic copolymer X were calculated based on the quantitative analysis of oxygen in the hydrophilic copolymer X using elementary analysis.

The value of the average polymerzation degree (n) of the alkylene glycol units in units A was calculated from the polymerization degree of the alkylene glycol units in units A measured by gel permeation chromatograhy.

Example 1:

A hydrophilic copolymer X comprising 60% by weight of hydroxyethyl monomethacrylate units as units A and 40% by weight of ethylene units as units B and having an intrinsic viscosity [n] of 0.19 dl/g as measured in xylene at 75° C and a high density polyethylene having a density of 0.965 g/cm^3 (Mitsubishi Polyethy JX-20, a product of Mitsubishi Petrochemical Co., Tm = 133° C) were blended in a ratio of 15 : 85 (by weight). The polymer blend was melt-kneaded in a melt extruder, pelletized and then dried.

Subsequently, the pellets were fed to a spinning machine where they were spun from a spinneret having 40 nozzles of 1.0 mm diameter at a spinning temperature of 155° C in the state that a spinning cylinder with a length of 2 m was provided right under the spinneret. The spinning was carried out at a spinning draft of 314 and a spinning speed of 250 m/min. The spun fibers were wound on bobbins.

The unstretched fibers thus obtained were heat-treated at 115° C for 24 hours under constant-length conditions in an atmosphere of nitrogen. The unstretched fibers had a degree of crystallinity of 62% and a degree of crystal orientation of 75%.

The unstretched fibers were cold-stretched at 25° C to an amount of stretching of 80% and then hot-stretched in a box having a length of 2 m and heated at 115° C until the total amount of stretching reached 520%. Thereafter, the stretched fibers were thermally set under relaxed conditions in a box having a length of 2 m and heated at the same temperature, so as to give a total amount of stretching of 400%.

The resulting porous fibers had a porous structure in which slit-like openings formed by lamellae and a number of longitudinally oriented fibrils interconnecting said lamellae were communicated with each other in the whole sections from the surface to the center of the fiber. It was very soft in hand feeling and had a porosity of 62.3%, a tensile strength of 3.38 g/d and a elongation of 50.5%.

Successively, 1 g. of the porous fibers were immersed in 200 c.c. of deionized water for 1 hour and then dehydrated by means of a centrifuge at 1,000 rpm for 5 minutes. The rate of weight increase was measured to determine the moisture content, which was found to be 135%.

Examples 2 and 3:

A hydrophilic copolymer X comprising 50% by weight of hydroxyethyl monomethacrylate units as units A and 50% by weight of ethylene units as units B and having an intrinsic viscosity $[\eta]$ of 0.19 dl/g as measured in xylene at 75° C and Mitsubishi Polyethy JX-20 used in Example 1 were blended in a ratio of 15 : 85 (by weight : Example 2) or 20 : 80 (by weight : Example 3). Then, the same procedure as in Example 1 was followed to obtain porous fibers.

These porous fibers had slit-like pores similar to those in Example 1 and possessed the properties given in Table 1.

Examples 4 and 5:

A hydrophilic copolymer X comprising 48 parts by weight of hydroxyethyl monomethacrylate units as units A, 52 parts by weight of ethylene units as units B and 2 parts by weight of vinyl acetate as units C and having an intrinsic viscosity $[\eta]$ of 0.19 dl/g as measured in xylene at 75° C and Mitsubishi Polyethy JX-20 used in Example 1 were blended in a ratio of 15 : 85 (by weight : Example 4) or 20 : 80 (by weight : Example 5). Then, the same procedure as in Example 1 was followed to obtain porous fibers.

These porous fibers had slit-like pores similar to those in Example 1 and possessed the properties given in Table 1.

Example 6:

A hydrophilic copolymer X comprising 45% by weight of polyethylene glycol monomethacrylate units which had an average polyethylene glycol polymerization degree (n) of 6 and 55% by weight of ethylene units and having an intrinsic viscosity [η] of 0.15 dl/g as measured in xylene at 75 °C and Mitsubishi Polyethy JX-20 used in Example 1 were blended in a ratio of 20 : 80 (by weight). Then, the same procedure as in Example 1 was followed to obtain a porous fiber.

The porous fiber had similar slit-like pores to those in Example 1 and possessed the properties given in Table 1.

Examples 7 and 8:

A hydrophilic copolymer X comprising 35 parts by weight of polyethylene glycol monomethacrylate units which had an average polyethylene glycol polymerization degree (n) of 6 and 65 parts by weight of ethylene units and having an intrinsic viscosity [η] of 0.15 dl/g as measured in xylene at 75 °C and Mitsubishi Polyethy JX-20 used in Example 1 were blended in a ratio of 20 : 80 (by weight : Example 7) or 25 : 75 (by weight : Example 8). Then, the same procedure as in Example 1 was followed to obtain porous fibers.

These porous fibers had slit-like pores similar to those in Example 1 and possessed the properties shown in Table 1.

Comparative Example 1:

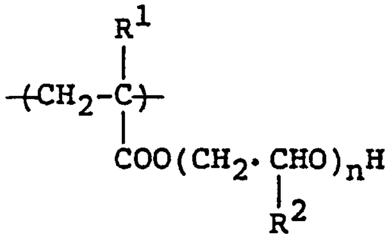
A porous polyethylene fiber was prepared in the same manner as in Example 1, using a high density polyethylene of Mitsubishi Polyethy JX-20 alone as the polymer. Its moisture content was measured at 6%.

Table 1

	Porosity (%)	Tensile strength (g/d)	Elongation (%)	Moisture content (%)
Example 1	62.3	3.38	50.5	135
Example 2	63.2	3.24	53.6	119
Example 3	58.5	3.44	48.3	151
Example 4	61.8	3.33	50.5	108
Example 5	58.0	3.36	46.7	139
Example 6	59.8	3.18	48.5	115
Example 7	61.5	3.05	50.2	76
Example 8	56.5	3.33	46.8	125

Claims

1. A porous fiber comprising a hydrophilic copolymer X composed principally of monomer units A represented by the following formula:



$$-\!\left(CH_2-\overset{\displaystyle R^1}{\underset{\displaystyle COO(CH_2\cdot \underset{\displaystyle R^2}{C}HO)_nH}{C}}\right)\!-$$

wherein R^1 and R^2 represent independently hydrogen or methyl and n is a number in the range of 1 to 9 and ethylene units B and a polyolefin Y and having a porous structure in which communicating pores are formed by lamellae and a large number of longitudinally oriented fibrils interconnecting said lamellae.

2. A porous fiber as claimed in Claim 1 wherein the weight ratio (X/Y) of the hydrophilic copolymer X to the polyolefin Y is in the range of 5/95 to 50/50.

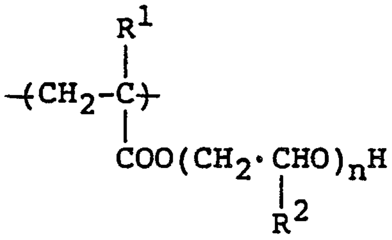
3. A porous fiber as claimed in Claim 1 or 2 wherein the weight ratio (A/B) of the units A to the units B in the hydrophilic copolymer X is in the range of 80/20 to 10/90.

4. A porous fiber as claimed in Claim 3 wherein the intrinsic viscosity of the hydrophilic copolymer X as measured in xylene at 75 °C is in the range of 0.07 to 0.40 dl/g.

5. A porous fiber as claimed in any one of Claims 1 through 4 wherein the polyolefin Y is polyethylene.

6. A porous fiber as claimed in any one of Claims 1 through 5 wherein the porosity, the tensile stregth and the elongation are in the range of 30 to 80%, 0.5 to 8 g/d and 1to 300%, respectively.

7. A process for the production of porous fibers which comprises the step of melt-spinning a blend of a hydrophilic copolymer X composed principally of monomer units A and ethylene units B and a polyolefin Y to form an unstretched fiber; and the step of heat-treating said unstretched fiber in a vacuum or an inert gas medium at a temperature not higher than the melting point of the polyolefin Y for a period of one hour or more and stretching the resulting fiber to make it porous, the monomer units A being represented by the following formula:



$$-\!\left(CH_2-\overset{\displaystyle R^1}{\underset{\displaystyle COO(CH_2\cdot \underset{\displaystyle R^2}{C}HO)_nH}{C}}\right)\!-$$

wherein R^1 and R^2 independently represent hydrogen or methyl and n is a number in the range of 1 to 9.

8. A process for the production of porous fibers as claimed in Claim 7 wherein the weight ratio (X/Y) of the hydrophilic copolymer X to the polyolefin Y is in the range of 5/95 to 50/50.

9. A process for the production of porous fibers as claimed in Claim 7 or 8 wherein the weight ratio (A/B) of the units A to the units B in the hydrophilic copolymer X is in the range of 80/20 to 10/90.

10. A process for the production of porous fibers as claimed in Claim 9 wherein the intrinsic viscosity $[\eta]$ of the hydrophilic copolymer X as measured in xylene at 75° C is in the range of 0.07 to 0.40 dl/g.

11. A process for the production of porous fibers as claimed in any one of Claims 7 through 10 wherein the polyolefin Y is polyethylene.

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP90/00890

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl^5 D01F6/46, D01F6/04, D01F6/30

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	D01F6/04, 6/30, 6/46

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

Jitsuyo Shinan Koho	1950 - 1990
Kokai Jitsuyo Shinan Koho	1971 - 1990

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	JP, B2, 51-20610 (Sekisui Chemical Co., Ltd.), 26 June 1976 (26. 06. 76), Claim, line 32, column 2 to line 18, column 3, lines 9 to 32, column 5, Example 2, drawings & JP, A, 47-16543	1 - 11
Y	JP, A, 47-16543 (Sanyo Chemical K.K.), 2 September 1972 (02. 09. 72), Claim, line 13, upper left column to line 15, lower right column, page 2, lines 9 to 12, upper right column, page 3 (Family: none)	1 - 11
Y	JP, A, 61-83305 (Mitsui Petrochemical Industries, Ltd.), 26 April 1986 (26. 04. 86), Line 14, lower left column, page 2 to last line, lower right column, page 4 & EP, A, 176350 & US, A, 4808367	1

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
September 25, 1990 (25. 09. 90)	October 15, 1990 (15. 10. 90)
International Searching Authority	Signature of Authorized Officer
Japanese Patent Office	

International Application No. PCT/JP90/00890

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

P	JP, A, 2-133607 (Mitsubishi Rayon Co., Ltd.), 22 May 1990 (22. 05. 90), Claim, line 11, upper right column, page 2 to line 4, lower left column, page 3, Example 1 (Family: none)	1 - 11

V.☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers .. . , because they relate to subject matter not required to be searched by this Authority, namely:

2.☐ Claim numbers . , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3.☐ Claim numbers ... . , because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI.☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1.☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.