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London WC2B 6UZ (GB)(54) **COMPOSITE FIBER HAVING POROUS SHEATH PART.**

(57) A composite fiber having a strength sufficient for practical use, easily going through carding process, and resistant to higher temperature when being processed into non-woven fabric or used as a non-woven fabric, which fiber is provided with a sheath part composed of porous polyolefin series synthetic resin and a non-porous core part. An apparent cross-sectional area of said sheath part is from 20 to 80 % of the entire cross-sectional area of the fiber. Said polyolefin series synthetic resin is preferably high density polyethylene or polypropylene. Said resin is made porous by mixing it with paraffin wax which is then removed after spinning process. The core part is selected from polypropylene resin, nylon of low melting point, and polyester of low melting point.

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The present invention relates to a composite fiber having a sheath part formed of porosized polyolefin-based synthetic resin, more particularly to a porous fiber having a fiber strength and processability with a carding machine, which may be put to practical use.

As synthetic fibers having fine pores, there are known porous polyester fibers and the like having waterabsorption properties used as fibers for cloth which are provided with water absorption properties in order to improve the comfort of wear. On the other hand, polyolefin-based fine porous fibers were developed for a variety of hollow fiber membranes for separation and used widely in the fields of medical equipment, industrial use and domestic use and the like. A number of these fine porous fibers have been developed, but there have been technical problems in controlling the shape or size of the pores.

For example, as a polyolefin-based porous fibers, there are known hollow fibers having strip-shaped voids in a so-called lamellar stack made by spinning polypropylene or polyethylene at a comparatively low temperature under high draft to obtain hollow type fibers, and heat-treating and then stretching them to a given ratio, or stretching them at an extremely low temperature. These fibers are, however, primarily used as hollow fiber membranes and the like and have a comparatively large denier and comparatively small pores so that they are not adequate for usages with make the most of functions such as liquid storage property and insulating property.

Therefore, the inventors have studied porous fibers having comparatively low denier and found that the strength of the fibers are lowered remarkably with the increasing void percentage of porous fibers, which results in practical problems. Namely, in the case of a highly porosized fiber, the strength is much reduced so that when processed into non-woven fabrics, woven fabrics and the like the strength of the obtained fabrics are low. Further, even with a porous fiber having a void percentage of 30 to 50% made of high-density polyethylene, it is difficult to impart crimps in the manufacture process of the fiber. Therefore, there is the problem that when processing by a carding machine, the connection of webs is poor due to the sinkage of the fibers in the cylinder of the carding machine and thus uniform carding is impossible.

For some uses heat-resistance is required, e.g. a polyethylene-based porous fiber should withstand use in boiling water and disinfection with steam. Further, when it is mixed with a binder fiber comprising a polyethylene fiber and a composite fiber of polyethylene/polypropylene, processed with a carding machine to obtain webs and passing it through a heat roller such as an embossing roller and a calender roller to obtain a heat bonded non-woven fabric, it is necessary to avoid decrease of the void percentage due to the shrinkage by heat and the shrinkage of the non-woven fabrics in the case of whole porous fiber. In the case of polypropylene-based porous fibers, a whole porous fiber is influenced by a shrinkage from a temperature of about 130 °C and the void percentage is lowered so that it is impossible to raise the surface temperature of the heat roller to 120 °C or more even if the web is made by mixing binder fibers and thus the productivity of non-woven fabrics is low.

Therefore, the inventors have developed a polyolefin-based porous fiber having strength for practical use and excellent ability to pass through a carding machine which may withstand a higher temperature when being processed into non-woven fabric or used as a non-woven fabric .

The composite fiber of the present invention comprises a sheath and core type composite fiber consisting of a sheath part formed of porosized polyolefin-based synthetic resin and a non-porous core part, and is basically characterized in that the apparent cross-sectional area of the sheath part is from 20 to 80% of the entire cross-sectional area of the fiber.

The polyolefin resin that can be used in the present invention is preferably polyethylene or polypropylene. When polyethylene is used, preferred is a high-density polyethylene (hereinafter referred to as "HDPE") having a melt flow rate (MFR) value, measured by a method according to ASTM D1238, of 0.3 to 20g/10 min. A preferred polypropylene is a polypropylene having a density of about 0.90 or more and an MFR value, measured by said measurement method, in the range of 0.5 to 20g/10 min.

If the MFR values deviate from the above ranges, the melt viscosity is incorrect when melt-spinning after the polyolefin resin is mixed with paraffin wax, and a problem arises in the spinning. The porosization of the sheath part is established by mixing paraffin wax essentially comprising saturated aliphatic or hydrocarbon compounds, spinning and extracting the paraffin wax by a solvent in melt-spinning of the sheath part.

The resin component used in the core part of the composite fiber of the present invention is a polyolefin resin such as a homopolymer or a copolymer such as high-density polyethylene or polypropylene and the like, or nylon having a low melting point or polyester having a low melting point, these melting points being different from that of the HDPE of the sheath part by less than 70 °C. Polypropylene homopolymer is preferable from the viewpoint of fiber physical properties and the suitability for composite spinning.

The ratio of cross-sectional area of the sheath to the core part should be controlled so that the apparent cross-sectional area of the sheath part is 20 to 80% of the entire cross-sectional area of the fiber. If the apparent cross-sectional area is less than 20%, the rate of the porous part is low and the function of the porous fiber cannot be fulfilled. If the apparent cross-sectional area exceeds 80%, the strength retention by the core part becomes insufficient and thus strength for practical uses can not be obtained.

The apparent cross-sectional area of the sheath part of the present invention is the cross-sectional area defined by the diameter of the sheath part and the perimeter of the core part containing the pore part. The entire cross-sectional area of the fiber is the sum of the above apparent cross-sectional area of the sheath part and the cross-sectional area of the core part.

The composite fiber having a porous sheath part of the present invention comprises a porous sheath part and a solid core part so that crimp impartment is sufficient since the crimp is imparted to the core part in crimp processing. Further, since the strength may be ensured by the core part and interlocking between the single fibers may be possible, previous problems in relation to carding suitability and strength may be solved.

Further, since the composite fiber of the present invention comprises a porous sheath part and a solid core part, the core part suppresses the shrinkage when heated. The shrinkage of the porous sheath part is smaller than that of a fiber consisting of a whole porous part and the decrease in the void percentage of the porous sheath part on heating is small. Thus the heat resistance of the overall composite fiber is improved.

The present invention will be explained by means of the following examples.

Example 1

After mechanically mixing 100 parts by weight of HDPE (Mitsui Petrochemical Industries, Co., Ltd.: Hi-zex 2200J) having an MFR value of 5.5g/10 min. and 100 parts by weight of paraffin wax (Nippon Oil Co., Ltd.: 135° Paraffin) having a density of 0.78g/cc and a melting point of 59 °C as raw materials of a sheath part, the mixture was put into a flat bottom vessel and the vessel was placed in a oven at 150 °C for 2.5 hours. After compatibilizing both materials uniformly, the mixture was cooled to solidify and powdered to prepare a material for melt-spinning.

As the raw material for the core part, polypropylene having a MFR value of 80g/10 min. (UBE KOSAN Co., Ltd.: TS365) was used. With a sheath-core type composite spinning machine comprising two extruders each having a screw diameter of 32mm and being equipped with 0.4mm×500 holes of nozzle for composite fibers, the extruder for the sheath part being fed by the material for the sheath part, an unstretched yarn having a denier of 10 was spun at a nozzle temperature of 170 °C at a spinning rate of 400m/min. with a ratio of cross-sectional areas of sheath part to core part of 5:5. The void percentage was about 15% when paraffin wax was extracted at this stage.

The unstretched yarn was combined to have about 20,000 denier and stretched to four times at 100 °C with stretching rollers at a rate of 8m/min. of a first stretching roller and at a rate of 32m/min of a second stretching roller and taken up by a bobbin.

The yarn which remained wound around the bobbin was then heat-treated at a constant length in an oven at 100 °C for one hour, and crimped with a stuffing box type crimper so as to impart 12 crimps/inch. The fiber was cut to about 51 mm to form staple fiber, and put into a soxhlet extractor to extract the paraffin wax in the sheath part by n-hexane to porosize the sheath part.

The thus obtained composite fiber had a denier of 2.5, a tensile strength of 2.59g/d, a tensile strain of 180%, a crimps number of 12.5 crimps/inch and a void percentage of 35.3%. The fiber was examined as to its ability to pass through a carding machine by passing it through a test carding machine (Yamato Kiko Co., Ltd.: SC-360 DR). This showed that it was excellent and that it was a practically usable fiber from the viewpoint of the strength. The void percentage was calculated by the following equation.

Void percentage (%) = (diameter denier - weight denier)/diameter denier × 100

diameter denier = $\pi/4R^2 \times \rho_0 \times 9000 \times 10^5$

R = apparent diameter after extraction of paraffin wax (cm)

ρ_0 = (core part weight + sheath part weight)/(core part volume + resin volume of sheath part)

Example 2

An unstretched yarn having a denier of 10 was spun in the same manner as in Example 1 using the same raw material for the sheath part and the same raw material for the core part except that the ratio of cross-sectional area of the sheath to core was 8:2 and the nozzle temperature was 160 °C. After the yarn was stretched, heat-treated, crimped and cut, it was placed in a soxhlet extractor in the same manner as in Example 1 to porosize the sheath part similarly.

The fiber thus obtained had a denier of 2.1, a strength of 1.96g/d, a strain of 86%, a crimp number of 13 crimps/inch and a void percentage of 48.8%. The fiber was examined as to its ability to pass through a carding machine. As a result, some hanging of web was observed as compared to Example 1, but the ability to pass was considered to be no problem.

Example 3 and 4

Fibers having a ratio of core part of 7:3 (Example 3) and a ratio of core part of 2:8 (Example 4) were spun using the same raw material for the sheath part as in example 1 and polypropylene having an MFR value of 48 (UBE KOSAN Co., Ltd.: ZS-1238) as a raw material for the sheath part. The spinning conditions of Examples 3 and 4 were the same as those in Example 1 except that the nozzle temperature in Example 4 was 200 °C.

The composite fiber thus-obtained in Example 3 had a denier of 2.2, a strength of 2.15g/d, a strain of 95% and a void percentage of 46.5%. The composite fiber thus-obtained in Example 4 had a denier of 3.1, a strength of 3.10g/d, a strain of 150% and a void percentage of 17.0%. Both had excellent aptitudes for the carding machine.

Example 5

A composite fiber was obtained in the same manner as in Example 1 except that an unstretched yarn having a denier of 10 was obtained using the same raw material for the sheath part as in Example 1 and a nylon having a low meltingpoint of 176 to 180 °C (UBE KOSAN Co., Ltd.: 3035U) for the core part at a ratio of the sheath to core of 5:5 at a nozzle temperature of 170 °C.

The composite fiber had a denier of 2.4, a strength of 2.36g/d, a strain of 180%, a void percentage of 33.8% and an excellent ability to pass through a carding machine.

Comparative Examples 1 and 2.

A porous fiber was obtained in the same manner as in Example 1 except that an unstretched yarn having a denier of 10 was spun using an extruder having a screw diameter of 25 mm and being equipped with 0.4mm x 160 holes of nozzle without using a composite spinning apparatus and then stretched to a stretch ratio of three times (Comparative Example 1), and four times (Comparative Example 2). The fiber thus-obtained in Comparative Example 1 had a denier of 2.2, a strength of 1.10g/d, a strain of 270% and a void percentage of 45%. The fiber thus-obtained in the Comparative Example 2 had a denier of 1.7, a strength of 1.74g/d, a strain of 130% and a void percentage of 37%. The abilities to pass through a carding machine of both fibers obtained in Comparative Examples 1 and 2 were quite poor so that separate carding was difficult.

Example 6

After mechanically mixing 100 parts by weight of polypropylene having a MFR value of 3g/10 min. (UBE KOSAN Co., Ltd.: YK 121) and 100 parts by weight of paraffin wax (Nippon Oil Co., Ltd.: 135 ° paraffin), the mixture was fed to a flat bottom vessel which was placed in an oven at 180 °C for 2.5 hours. After compatibilizing both materials uniformly, the mixture was cooled to solidify and powdered to prepare a raw material for a sheath part for melt-spinning.

As a material for the core part, polypropylene having an MFR value of 48 (UBE KOSAN Co., Ltd.: ZS-1238) was used. With a sheath-core type composite spinning machine consisting of two extruders having a screw diameter of 32mm and being equipped with composite nozzle of 0.4mm x 500 holes, the extruder for the sheath part was fed by the raw material for the sheath part, an unstretched yarn having a denier of 10 was spun at a nozzle temperature of 200 °C, at a spinning rate of 400m/min. with a ratio of cross-sectional areas of sheath part to core part of 8:2.

The unstretched yarn was combined to have a denier of about 20,000 and stretched to four times at 100 ° C with stretching rollers at a first stretching roller rate of 8m/min, and at a second stretching roller rate of 32m/min and taken up by a bobbin.

Then the fiber which remained wound around the bobbin was heat-treated at a constant length for one hour in an oven at 130 ° C, and crimped with a stuffing box type crimper so as to impart 12 crimps/inch. The fiber was then cut to about 51 mm to form staple fibers, and put into a soxhlet extractor to extract the paraffin wax in the sheath part from n-hexane to porosize the sheath part.

The thus obtained composite fiber had a tensile strength of 2.2, a strain of 360% and a void percentage of 25%. The carding characteristics were excellent.

Comparative Example 3

A porous fiber was obtained in the same manner as in Example 6 except that an unstretched yarn was spun having a denier of 10 at a nozzle temperature of 175 ° C with a extruder having a screw diameter of 25mm being equipped with a nozzle of 0.4mm×160 holes, using the material for the sheath part as used in Example 6 and without the composite spinning system and that the stretch ratio of the yarn was three times. The fiber thus obtained had a strength of 1.9g/d, a strain of 450% and a void percentage of 26%.

The spinning conditions and physical properties of the above Examples and Comparative Examples are outlined in the following Table 1.

TABLE 1

	raw material		ratio of sheath to core part	spinning condition		denier of unstretched fiber	stretch ratio	void ratio	property		carding property
	seath part	core part		nozzle temperature	spinning rate				strength	strain	
Ex. 1	HDPE/Pa=50/50wt%	P.P. (Ml=80)	5/5	170 °C	400/min	10denier	4.0times	35.3%	2.59g/d	150%	○
Ex. 2	"	"	8/2	160	"	"	"	48.8	1.96	86	○
Ex. 3	"	P.P. (Ml=48)	7/3	170	"	"	"	46.5	2.15	95	○
Ex. 4	"	"	2/8	200	"	"	"	17.0	3.10	150	○
Ex. 5	"	low melting point nylon	5/5	170	"	"	"	33.8	2.36	180	○
Comp. 1	"	—	10/0	145	200	"	3.0	45.0	1.10	270	×
Comp. 2	"	—	10/0	145	200	"	4.0	37.0	1.74	130	×
Ex. 6	PP/Pa=50/50wt%	P.P. (Ml=80)	8/2	200 °C	400	"	3.0	25	2.2	360	◎
Comp. 3	"	—	10/0	175	200	"	3.0	26	1.9	450	○

Pa: Paraffin wax P.P: Polypropylene carding property: ○ . . . excellent × . . . poor

55 Test for heat resistance

The fibers obtained in Examples 2 and 6 and Comparative Examples 1 and 3 were placed in an oven at a temperature of 80 to 130 °C for 30 min. and the change of the void percentages before and after heating

was measured. The following Table 2 shows the results of the measurements.

Table 2

	untreated	80 ° C	100 ° C	120 ° C	130 ° C	140 ° C
Ex. 1	48.8	44.0	35.8	31.0	melt	-
Comp. 1	45.0	40.8	33.6	18.5	melt	-
Ex. 6	25	25	24	22	18	10
Comp. 3	26	26	25	21	10	5

As seen from the results shown in Table 2, The decreases of the void percentages of the fibers obtained in Examples were small and thus they had an excellent heat resistance since the solid core parts control the shrinkage.

As understood also from the Table 1, the fibers obtained in the Examples had equal or more void percentages even though the paraffin wax contents were small. For example, the fibers of Example 2 had a void percentage of 48.8% at 40% of paraffin wax. On the other hand, the fibers of Comparative Example 1 had a void percentage of 45 % at 50% of paraffin wax, i.e. the sheath part of the Example 2 had a void percentage of 61%. The reason may be considered as follows. It is estimated that since a polypropylene component having a high melting point was added when spinning there is a need to raise the spinning temperature so that the porous sheath part is spun in the direction towards the less cooled part to slowly could in spinning, and then the growth of lamellar crystals is promoted.

On the other hand, in the case of Comparative Example 1, a spun yarn having a single PE porous part was obtained so that increasing the nozzle temperature and moderating the cooling conditions deteriorate the spinning properties or cause an increase the denier unevenness; this is not preferable. As to the composite fiber obtained in Example 6, the heat resistance is high so that use as a filter for liquid used in boiling water is expected and that it may be possible to be sterilized at high temperature (130 ° C) by an autoclave.

As described above, composite fibers having a sheath part according to the present invention have a high strength, an improved aptitude for carding and a resistance to high temperature so that they may be used as a raw material for filters for high temperature liquids and for non-woven fabrics which may be sterilised at a high temperature.

Claims

1. A composite fiber comprising a porous sheath part which is formed of a porosized polyolefin-based synthetic resin and a non-porous core part, the apparent cross-sectional area of said sheath part being 20 to 80% of the entire cross-sectional area of the composite fiber.
2. A composite fiber as claimed in claim 1, wherein said polyolefin-based synthetic resin is a high density polyethylene.
3. A composite fiber as claimed in claim 1, wherein said polyolefin-based synthetic resin is polypropylene.
4. A composite fiber as claimed in any one of claims 1 to 3, wherein the porosization has been carried out by mixing the polyolefin-based resin and paraffin wax, spinning and then removing the paraffin wax.
5. A composite fiber as claimed in any one of claims 1 to 4, wherein said core part is formed of polypropylene resin.
6. A composite fiber as claimed in any one of claims 1 to 4, wherein said core part is formed of nylon resin having a low melting point.
7. A composite fiber as claimed in any one of claims 1 to 4, wherein said core part is formed of polyester resin having a low melting point.
8. A non-woven fabric comprising a multiplicity of composite fibers as claimed in any one of the preceding claims.

9. A filter for liquids comprising a multiplicity of composite fibers as claimed in any of claims 1 to 7.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/JP92/00261

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl ⁵ D01F8/06, D04H1/42//D01F6/04, 6/46		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC	D01F1/00-8/18, D04H1/42	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
Jitsuyo Shinan Koho	1926 - 1992	
Kokai Jitsuyo Shinan Koho	1926 - 1992	
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹		
Category *	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	JP, A, 59-76919 (Chisso Corp.), May 2, 1984 (02. 05. 84), Claim, upper column, page 2, example 5 (Family: none)	1-3, 5
Y	JP, A, 59-43118 (Chisso Corp.), March 10, 1984 (10. 03. 84), Claim, line 15, upper left column, page 2 to line 11, lower right column, page 3, examples 1 to 7, drawings (Family: none)	1, 3, 5
Y	JP, B2, 62-44046 (Mitsubishi Rayon Co., Ltd.), September 18, 1987 (18. 09. 87), Claim, pages 3 to 4, example (Family: none)	1-3
Y	JP, B1, 44-14891 (Toray Industries, Inc.), July 2, 1969 (02. 07. 69), Column 2, page 1 to column 4, page 2 (Family: none)	1, 6
* 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	
June 5, 1992 (05. 06. 92)	June 16, 1992 (16. 06. 92)	
International Searching Authority	Signature of Authorized Officer	
Japanese Patent Office		

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	JP, A, 60-28565 (Chisso Corp.), February 13, 1985 (13. 02. 85), Claim, line 8, lower left column, page 2 to line 10, upper left column, page 3, examples 5 to 12 (Family: none)	1, 3, 7
A	JP, B2, 2-40764 (Mitsui Petrochemical Industries, Ltd.), September 13, 1990 (13. 09. 90), Claim, line 9, column 3, page 2 to line 43, column 6, page 3 (Family: none)	4

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