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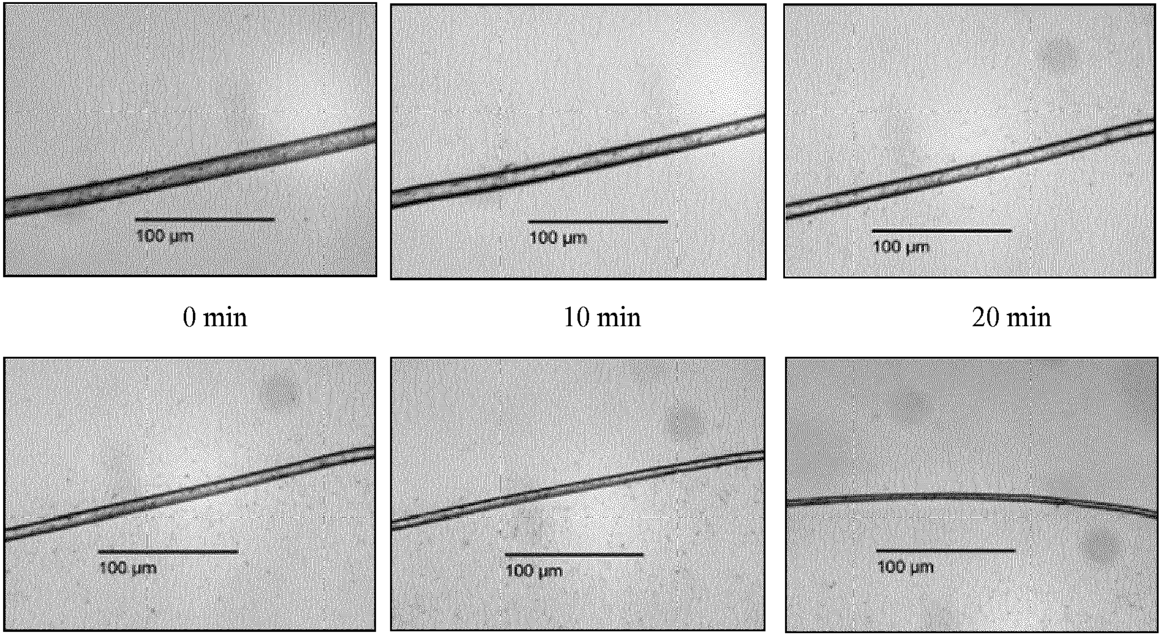
(54) POLYAMIDE FIBRE

(57) Method of partially swelling a polyamide fibre, wherein a core region of the fibre remains essentially free of water and the surface structure of the fibre is water swollen, wherein the polyamide fibre is exposed to a mixture comprising calcium chloride, ethanol and water, wherein the calcium chloride content is > 6 mol%, the ethanol content is < 25 mol% and the ratio between water and ethanol is > 2.5.

Fig. 1



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Description

[0001] The present invention relates to a method of partially swelling a polyamide fibre, wherein a core region of the fibre remains essentially un-swollen and the surface structure of the fibre is swollen. The invention further relates to a polyamide fibre, comprising a core region and a swollen surface structure. Finally, the invention relates to different uses of such fibres.

BACKGROUND OF THE INVENTION

[0002] The use of polyamide fibres in textiles is well known in the art. In general, polyamide fibres are produced by a melt spinning process and exhibit high strength, abrasion resistance and dimensional stability. Textile applications of polyamide fibres include clothing but also technical and heavy duty textiles as well as usage in reinforcing fibres in polymer fibre composites. In general polyamide fibres show smooth surfaces with low surface energy and high chemical inertness due to the fibre manufacturing technologies. This feature, however, makes the use of polyamide fibres unsuitable for applications requiring better adhesion to other substances, for example polymer matrices in polymer fibre composites or higher sorption capability of fibres.

[0003] The general purpose of surface modification of fibres is to alter the physical, chemical or biological properties of the native surface. Surface engineering is the discipline that addresses the modification of surfaces especially of solid materials. There is big interest on the modification of the surface without affecting the bulk properties. Characteristics like hydrophobicity, adhesion, hardness, permeability, friction factor, bacterial repellence, surface conductivity, and biocompatibility can be modified. Other properties like dyeability, wettability and biocompatibility can also be changed by varying the properties and the structure of the surface. Another aspect could be the formation of a hydrophobic fibre coating or introduction of a micro-structure onto the surface to implement hydrophilicity to the fibre. There are different methods by which the modification of the surface of polyamide fibres can be accomplished. There has already been some research on plasma modification, heat treatment, chlorosulfonation, polymerization etc. to change the amount of endgroups at the surface.

[0004] However, all these methods are either complicated or require high energy consumption or chemicals which may impact the environment negatively.

[0005] It is also known in the literature that a mixture of calcium chloride, water and ethanol ($CaCl_2/H_2O/EtOH$) in a defined composition acts as a solvent for polyamide and other fibres. Ngo and Bechtold reported the use of calcium chloride/ethanol/water solution to dissolve fibroin followed by a regeneration step (Journal of Applied Polymer Science (2016), 133(35)). CN 102560888 discloses the use of calcium chloride/ethanol/water solution to prepare vitamin E loaded silk fibroin nanofiber membranes.

[0006] The effect of calcium chloride on the surface properties of Kevlar fibre was investigated by Li, Zhen, Luo and Lu (In [Journal of Applied Polymer Science (2015), 132(4), 41358/1-41358/8],). The surface of Kevlar fibre was treated by calcium chloride / ethanol solution at the boiling point of ethanol of 79°C.

BRIEF DESCRIPTION OF THE INVENTION

[0007] So far the available treatments of the surface of polyamid fibres either yield insufficient surface modifications or they yield in the dissolution of the fibre and thus in the loss of the fibre properties.

[0008] It is therefore the object of the present invention to provide a polyamide fibre with improved surface properties that still exhibits sufficient strength as an unmodified fibre.

[0009] This object is solved by a method of swelling the surface of a polyamide fibre, wherein the polyamide fibre is exposed to a mixture comprising calcium chloride, ethanol and water, wherein the calcium chloride content is > 6 mol%, the ethanol content is < 25 mol% and the molar ratio (moles / moles) between water and ethanol is > 2.5.

[0010] The invention also deals with a swollen polyamide fibre obtainable by a method as described.

[0011] By treating a polyamide fibre with this mixture it is possible to obtain a polyamide fibre that is swollen and exhibits improved surface properties regarding moisture uptake and water retention and that has an increased surface area. In order to maintain the bulk properties of the untreated polyamide fibre it is preferred that the untreated polyamide fibre is exposed to the mixture for only such a time that a core region of the polyamide fibre remains essentially untreated (= intact) and only the surface structure of the fibre is swollen.

[0012] All reported works investigating mixtures comprising calcium chloride, ethanol and water aim at the dissolution of the polymers or fibres in the mentioned calcium chloride, ethanol and water solution, but not the use of such solvents for the modification of fibre surface.

[0013] The present invention is directed to a novel surface structure of polyamide fibres. More particularly, the novel surface structure is achieved by modifying the fibres with an environmental friendly solution of calcium chloride, ethanol and water mixtures at ambient temperature (25 °C). The swollen fibre surface structure exhibits excellent liquid sorption capability.

[0014] With this method a specifically defined fibre surface structure is achieved wherein the fibre surface is swollen and the fibre core remains intact. The relative thickness of the swollen surface layer of the polyamide fibres ranges from 50% to 250% based on the virgin fibre diameter.

[0015] In a preferred embodiment the mixture comprises 8 mol% to 20 mol% calcium chloride, 9 mol% to 21 mol% ethanol and the ratio between water and ethanol content is > 2.5, preferably the mixture comprises 9 mol% to 19 mol% calcium chloride, 10 mol% to 20 mol% ethanol and the ratio between water and ethanol content is > 2.5, more preferably the mixture comprises 10 mol% to 18 mol% calcium chloride, 11 mol% to 19 mol% ethanol and the molar ratio between water and ethanol content is > 2.5.

[0016] For carrying out the method it is preferred that the fibre is exposed to the mixture by soaking or padding.

[0017] The invention provides a polyamide fibre, comprising a core region and a swollen surface structure.

[0018] The core region is the part of the polyamide fibre that is non-treated and therefore non-modified or non-swollen. It exhibits the bulk properties of the untreated or virgin polyamide fibre. The swollen region has a smaller density than the untreated fibre. In particular the density of the core region (untreated region of the fibre, i.e. the part of the fibre not exposed to the mixture) is higher than of the swollen region. Typically, the core region shows the same density as the type of polyamide fibre used. If e.g. the untreated fibre is polyamide 66 with a density of 1.13 g/cm^3 then also the core region has this density whereas the swollen region has a lower density. This can be observed under a microscope as shown in the figures below.

[0019] The relative thickness of the water swollen surface structure of the polyamide fibre ranges from 50 % to 250 % based on the non-treated fibre diameter.

[0020] In a preferred embodiment the fibre is characterised in that the ratio between the total diameter and the diameter of the core region is >1.

[0021] In a preferred embodiment the polyamide fibre is characterised by a mass change of > 15 wt.%, preferably of > 30 wt.%, more preferably of > 65 wt.% by exposure to 90% relative humidity at 25 °C. This mass change is an increase of mass by water vapour adsorption by the fibre.

[0022] The water vapor adsorption was measured gravimetrically with an automated multisampling moisture sorption analyzer SPS11 (ProUmid, Germany-Ulm) at 25 °C. The samples were conditioned at 25 °C and 40% relative humidity (RH). Then the relative humidity was reduced to 0% and the sorption and desorption cycles were started. The steps for the increase and decrease in RH were 10%, from 0 to 95% RH. The mass of the sample was measured every 10 min and the equilibrium condition was set to a mass change of 0.003 % per 60 min. Once the equilibrium was reached the RH was increased/decreased to the next step. The minimum time was 120 min and the maximum time 48 h for one cycle.

[0023] In an embodiment the polyamide fibre is characterised by a water retention value of > 30 wt.%, preferably of > 75 wt.%, more preferably of > 100 wt.%.

[0024] The water retention was measured as follows: After the treatment and the unravelling the fibers were conditioned in a climate room with 20°C +/- 2 °C and 65% +/- 4% RH for at least 24 h. Then the fibers were weighted to determine the mass of the conditioned fibers (m_c). Afterwards they were soaked in deionized water for 24h. For the water retention value the water soaked samples are placed into a plastic centrifuge tube with a filter inside. The samples were centrifuged at 2500 G with 4410 rpm for 10 min with a Heraeus Multifuge. The wet mass of the samples (m_w) is weighted after the centrifugation. For completion of the determination the samples are dried at 105 °C for 4h and then they are put into a desiccator to cool down for 24h. Then the samples are reweighted.

[0025] The invention also concerns a textile, comprising a polyamide fibre according to the aforementioned kind.

[0026] The textile can be woven, knitted or non-woven or it is a yarn or a rope.

[0027] It is possible to use the obtained fibres for different applications. E.g. the use of the polyamide fibre or the textile for storing and releasing liquids in pharmaceutical applications is possible. This can e.g. be in drug delivery.

[0028] A further use of the polyamide fibre or the textile is for absorbing or anchoring chemical substances with additional functionalities onto the fibre surface.

[0029] Still a further use of the polyamide fibre or the textile is for a better absorbance of dyes.

[0030] Alternatively, textile applications requiring high moisture sorption capability like underwear etc. are possible.

[0031] Another use is for enhancing the seam strength by adhesive and thermal bonding of textiles.

[0032] Further details and advantages are provided below and in reference to examples and figure.

Fig. 1	shows dissolving polyamide fibre in mixture solution of 12.5 mol% calcium chloride, 25 mol% water and 62.5 mol% ethanol (Sample CE17 with water/ethanol ratio of 0.4).
Fig. 2	shows swelling polyamide fibre in mixture solution of 12,5 mol% calcium chloride, 68.75 mol% water and 18.75 mol% ethanol (Sample E2 with water/ethanol ratio of 3,67).
Fig. 3	shows the difference in pore size of polyamide fabrics before (Fig. 3a) and after modification (Fig. 3b) in mixture solution of 12.5 mol% calcium chloride, 68.75 mol% water and 18.75 mol% ethanol.

[0033] There is a solubility border of calcium chloride of above 20 mol% in the ethanol / water solution based on 100 mol% of the total composition of ethanol, water and calcium chloride. Thus this concentration range of calcium chloride is not the objective of the current invention. Is the calcium chloride content above 6 mol%, the ethanol content below or equal 25 mol% and ratio between water and ethanol content is above 2.5, the mixture of calcium chloride, water and ethanol does not dissolve nor swell the polyamide fibre (non-solvent, Comparative examples CE18-CE21, see table 1).

[0034] Is the calcium chloride content below 6 mol%, the ethanol content above 25 mol% and the ratio between water and ethanol content is below 2.5, the mixture of calcium chloride, water and ethanol does not dissolve nor swell the polyamide fibre (non-solvent, Comparative examples CE22-CE26).

[0035] Is the calcium chloride content above 6 mol%, ethanol content above or equal 25 mol% and ratio between water and ethanol content is below or equal 2.5, the fibre surface is dissolved in the solution and a reduction of the fibre diameter Da(t) is observed (Comparative examples CE7-CE17), Table 2, Fig. 1).

[0036] The swelling of the fibre surface, and thus leading to the novel modified fibre structure, is achieved only with solutions having following compositions: a calcium chloride content above 6 mol%, a ethanol concentration bellow 25 mol% and a ratio between water and ethanol content above 2.5 (Examples E1 to E6, Fig. 2).

[0037] Preferable suitable solvents for achieving the novel fibre structure is comprising of 8 mol% to 20 mol% calcium chloride, 9 mol% to 21 mol% ethanol and the ratio between water and ethanol content is above 2.5 whereas the sum of all three components make 100 mol%.

[0038] More preferable suitable solvents for achieving the novel fibre structure is comprising 9 mol% to 19 mol% calcium chloride, 10 mol% to 20 mol% ethanol and the ratio between water and ethanol content is above 2.5 whereas the sum of all three components make 100 mol%.

[0039] Even more preferable suitable solvents for achieving the novel fibre structure is comprising of 10 mol% to 18 mol% calcium chloride, 11 mol% to 19 mol% ethanol and the ratio between water and ethanol content is above 2,5 whereas the sum of all three components make 100 mol%.

[0040] The modified fibre structure exhibits excellent liquid sorption capability. The moisture uptake of the novel modified fibre structure in the sorption equilibrium experiments reaches a level of over 100 % in 95% relative humidity which is much higher than the referent virgin polyamide fibre (9.77 %) and polyamide fibre modified with referent dissolving solvent (11.33 %), (Table 4). The excellent sorption behaviour makes the novel fibre structure suitable for storing and releasing liquids in pharmaceutical applications like drug delivery. Furthermore, the swollen surface and its high sorption capability would also allow the use of the novel fibre structure for absorbing and anchoring chemical substances with additional functionalities onto the fibre surface as well as dyes (Table 5).

[0041] The method with the specific calcium chloride, ethanol and water solution can be applied to all textile fabrics produced by known textile technologies such as weaving, knitting but also to nonwoven structures as well as yarn and rope structures which is manufactured from polyamide fibres. The formation of the swollen surface of the polyamide fibre in a textile fabric, nonwoven, yarn etc. leads to the same advantages in sorption behaviour of the fabrics as found by the polyamide fibres above. It allows the use of polyamide fabrics in textile application requiring high moisture sorption capability like underwear etc. Furthermore, the swollen surface of textiles fabrics will also enhance the seam strength by adhesive and thermal bonding of textiles.

[0042] For the modification of polyamide fibres and/or textile fabrics and/or yarns, ropes etc., following modification procedures can be applied. The fibres or fabrics are soaked in a solvent bad for a desired time to achieve the desired relative thickness of the swollen surface layer. The time can range from few seconds up to one hour. Then the fibres and/or fabrics and/or yarns etc. are taken out of the solvent bad, undergo further washing step with fresh water followed by drying either at ambient temperature or in drying oven.

[0043] Alternatively, any wet textile padding processes can be applied to bring the fibres and/or fabrics etc. in contact with the solvent mixture of calcium chloride, water and ethanol such as Foulard, J-Box etc. followed by continuous washing and drying processes which is known to the persons in the art.

[0044] According to another basic embodiment the swollen fibre structure reduces the distances between the fibre and yarns in the textile fabric structures thus the pore size (Fig. 3, taken by stereo light microscope). Hence the modification techniques can be used to control the water and air permeability through the textile structure.

Observation of swelling and dissolution of polyamide fibre

[0045] Fibres were placed onto an object slide and treated by covering the fibres with the solution. It was covered with another object slide to prevent the evaporation of ethanol. Every five minutes a picture of the ongoing treatment was taken. The mixture solutions are categorised in 3 classes: a) non-solvent when no change in fibre diameter is observed (Table 1, Comparative examples CE18-CE26; b) dissolving when a decrease of the outer fibre diameter is observed (Table 1, Comparative examples CE7-CE17, Fig. 1) and c) swelling when a new structure of fibre is formed and an increase of the outer fibre diameter is observed whilst the inner fibre diameter is reduced (Table 1, Examples E1-E6, Fig. 2).

Measurement of fibre diameter during solvent treatment with calcium chloride, water and ethanol mixture

[0046] Fibres were placed onto an object slide and treated by covering the fibres with the solution. It was covered with another object slide to prevent the evaporation of ethanol. With a magnification of 10, pictures were taken under the light microscope and the fibre diameters were determined up to a treatment time of 50 minutes. The change in fibre diameter $\Delta D(t)$ is defined as the different of the fibre outer diameter after a modification Da(t) after a time period t and the virgin fibre diameter D(0):

$$\Delta D(t) = Da(t) - D(0) \text{ in } \mu m$$

[0047] A positive ΔD value indicates the swelling of the fibre surface, whilst a negative value of ΔD indicates the dissolution of the fibre surface.

[0048] The relative thickness of the swollen surface layer Hs(t) is determined by the difference between the outer diameter Da(t) and the inner diameter Di(t) of the fibre:

$$Hs(t) = [Da(t)\text{-}Di(t)/D(0)]*100\%$$

Moisture adsorption measurement

[0049] The water vapour adsorption was measured gravimetrically with an automated multisampling moisture sorption analyzer SPS11 (ProUmid, Ulm, Germany) at 25 °C. The samples were conditioned at 25 °C and 40% relative humidity (RH). Then the relative humidity was reduced to 0% and the sorption and desorption cycles were started. The steps for the increase and decrease in RH were 10%, from 0 to 95% RH. The mass of the sample was measured every 10 min and the equilibrium condition was set to a mass change of 0.003 % per 60 min. Once the equilibrium was reached the RH was increased/decreased to the next step. The minimum time was 120 min and the maximum time 48 h for one cycle. Five samples were measured. The untreated fibres as a reference, fibres treated with solution CE-17 for 10 min and 15 min and fibres treated with solution E-2 for 10 min and 15 min.

Sample preparation for moisture and dye sorption experiments on fibres

[0050] A specified amount of fibres was weighted and put into a glass bottle. Then the solution for the treatment was added so that all the fibres were immersed in the solvent. After specific time ranges the fibre bundle was taken out of the bottle and put into water to remove the whole solvent. The bundle was washed several times with deionised water to remove the remaining solution. Then the bundle was allowed to dry.

Fabric treatment

[0051] Fabrics were cut into small pieces to fit into the petri dishes. Samples with around 300 mg were obtained. Afterwards the samples were put into the petri dishes and overlaid with the solvents for 30 minutes. After the treatment, the samples were immersed in water for approximately 10 min. followed by washing with fresh water. Then they were allowed to dry.

Dye sorption

[0052] The treated fibres were dyed in a dyeing solution of DR81 (Direct Red 81 from Sigma Aldrich). The dyeing solution was prepared by weighing 100 mg of DR81 and then filling it up to 11 with water. The solution was put in a water bath with 80 °C for 30 min. Afterwards a serial dilution of the main solution was made to get the concentrations of 20, 40, 60, 80 and 100 mg/l dye in water. For every concentration a double determination was performed. The ratio of sample to dyeing solution was 1:100. The treated samples were dyed at 80 °C for 1 hour. After dyeing, the samples were washed 3 times with cold water. The remaining solution was allowed to cool down to do the photometry measurements afterwards. The Photometry was conducted on a Analytik Jena Specord Spectrophotometer.

Water retention value (WRV)

[0053] The fibres were conditioned in a climate room with 20°C +/- 2 °C and 65% +/- 4% RH for at least 24 h. Then the fibres were weighted to determine the mass of the conditioned fibres (m_c). Afterwards they are soaked in deionized water for 24h. For the water retention value the water soaked samples are placed into a plastic centrifuge tube with a filter inside. The samples were centrifuged at 2500 G with 4410 rpm for 10 min with a Heraeus Multifuge. The wet mass of the samples (m_w) is weighted after the centrifugation. For completion of the determination the samples are dried at 105 °C for 4h and then they are put into a desiccator to cool down for 24h. Then the samples are reweighted.

$$WRV = \frac{m_w - m_c}{m_c} * 100$$

WRV	water retention value / %
m_w	mass of wet samples / g
m_c	mass of conditioned samples / g

Examples

[0054]

Table 1: Calcium chloride, water and ethanol solvent compositions

Sample	$CaCl_2$ / mol%	H_2O / mol%	EtOH / mol%	H_2O/EtOH	Note
E1	10.00%	70.00%	20.00%	3.50	swelling
E2	12.50%	68.75%	18.75%	3.67	swelling
E3	13.33%	73.33%	13.33%	5.50	swelling
E4	17.16%	62.13%	20.71%	3.00	swelling
E5	18.00%	69.50%	12.50%	5.56	swelling
E6	11.11%	77.78%	11.11%	7.00	swelling
CE7	8.33%	58.33%	33.33%	1.75	dissolving
CE8	12.50%	56.25%	31.25%	1.80	dissolving
CE9	12.50%	62.50%	25.00%	2.50	dissolving
CE10	15.20%	30.40%	54.40%	0.56	dissolving
CE11	15.97%	49.28%	34.75%	1.42	dissolving
CE12	6.64%	40.37%	52.98%	0.76	dissolving
CE13	16.50%	27.00%	56.50%	0.48	dissolving
CE14	12.50%	12.50%	75.00%	0.17	dissolving
CE15	19.00%	12.50%	68.50%	0.18	dissolving
CE16	6.25%	18.75%	75.00%	0.25	dissolving
CE17	12.50%	25.00%	62.50%	0.40	dissolving
CE18	8.33%	75.00%	16.67%	4.50	non-solvent
CE19	8.33%	66.67%	25.00%	2.67	non-solvent
CE20	10.00%	85.00%	5.00%	17.00	non-solvent
CE21	6.36%	78.32%	15.32%	5.11	non-solvent
CE22	3.94%	48.57%	47.49%	1.02	non-solvent
CE23	0.00%	46.01%	53.99%	0.85	non-solvent
CE24	4.63%	28.50%	66.88%	0.43	non-solvent
CE25	4.80%	22.30%	72.90%	0.31	non-solvent
CE26	3.70%	10.00%	86.30%	0.12	non-solvent

Table 2: Dissolving polyamide fibre in mixture solution of 12,5 mol% calcium chloride, 25 mol% water and 62.5 mol% ethanol (Sample CE17 with water/ethanol ratio of 0.4)

Time / min	ΔD / μm	Da / μm
0	0.000	15.16
5	-0.657	14.50
10	-1.840	13.32
15	-2.614	12.55
20	-3.816	11.34
25	-4.584	10.58
30	-5.918	9.24
35	-7.060	8.10
40	-7.984	7.18
45	-9.400	5.76
50	-10.894	4.27

Table 3: Swelling polyamide fibre in mixture solution of 12.5 mol% calcium chloride, 68.75 mol% water and 18.75 mol% ethanol (Sample E2 with water/ethanol ratio of 3.67)

Time / min	ΔD / μm	Da / μm	Di / μm	[Da(t)-Di(t)/D(0)]*100 / %
0	0.00	15.61		
5	7.45	23.06	13.09	63.85
10	12.02	27.63	10.28	111.16
15	14.12	29.73	7.73	140.95
20	15.68	31.29	5.16	167.39
25	16.53	32.14	3.87	181.09
30	17.35	32.26	1.26	198.56
35	16.79	32.37		207.32
40	18.56	34.65		221.94
45	18.96	35.14		225.08
50	17.93	34.11		218.51

Table 4: Moisture sorption (mass change by moisture adsorption in % as function of relative humidity in %) of virgin polyamide fibre, fibre modified with mixture solution CE17 for 15 min and fibre modified with mixture solution E2 for 15 min.

Humidity / %	Mass change of virgin PA fibre / %	Humidity / %	Mass change of modified fibre using CE17	Humidity / %	Mass change of modified fibre using E2
0	0	0	0	0	0
5.04	0.496	4.93	0.542	5.04	2.332
9.98	0.827	9.98	0.893	9.98	3.702
20.04	1.436	20.14	1.508	20.04	6.106

(continued)

Humidity / %	Mass change of virgin PA fibre / %	Humidity / %	Mass change of modified fibre using CE17	Humidity / %	Mass change of modified fibre using E2
30.09	1.999	29.99	2.064	29.99	8.173
39.84	2.557	40.04	2.65	39.94	10.192
49.99	3.151	49.99	3.28	50.09	12.668
60.04	3.921	60.04	4.085	60.04	16.971
70.02	5.027	70.12	5.329	70.02	23.966
80.01	6.453	80.12	6.925	80.12	35.745
89.8	8.468	89.4	9.59	89.6	66.274
94.1	9.77	94.2	11.332	94.1	103.293

Table 5: Dye sorption behaviour (remaining dye concentration in the dyeing solvent as function of starting dye concentration in the dyeing solvent) of virgin polyamide fibre, fibre modified with mixture solution CE17 for 10 min and fibre modified with mixture solution E2 for 10 min. (The lower the remaining dye concentration, the higher the dye sorption capability of the fibre)

Starting dye concentration / mg/l	Remaining dye concentration for virgin PA fibre / mg/l	Remaining dye concentration for modified fibre using CE17 / mg/l	Remaining dye concentration for modified fibre using E2 / mg/l
20.00	0.56	0.43	0.91
40.00	1.10	0.87	1.38
60.00	1.89	1.45	1.98
80.00	2.97	2.40	2.40
100.00	3.97	3.35	3.02

Table 6: Water retention value of fibers treated with E 2 and CE 17 for 10 min

	virgin PA 66 fiber	modified fiber using CE 17	modified fiber using E 2
WRV/%	15.06 ± 1.36	16.54 ± 0.54	109.03 ± 3.63

Claims

1. Method of swelling the surface of a polyamide fibre, wherein the polyamide fibre is exposed to a mixture comprising calcium chloride, ethanol and water, wherein the calcium chloride content is > 6 mol%, the ethanol content is < 25 mol% and the molar ratio between water and ethanol is > 2.5.

2. Method according to claim 1, **characterised in that** the mixture comprises of 8 mol% to 20 mol% calcium chloride, 9 mol% to 21 mol% ethanol and the ratio between water and ethanol content is > 2.5, preferably the mixture comprises 9 mol% to 19 mol% calcium chloride, 10 mol% to 20 mol% ethanol and the ratio between water and ethanol content is > 2.5, more preferably the mixture comprises 10 mol% to 18 mol% calcium chloride, 11 mol% to 19 mol% ethanol and the molar ratio between water and ethanol content is > 2.5.

3. Method according to claim 1 or claim 2, **characterised in that** the fibre is exposed to the mixture by soaking or padding.

4. Polyamide fibre, comprising a core region and a swollen surface structure.

5. Polyamide fibre according to claim 4, **characterised in that** the surface structure comprises pores.

6. Polyamide fibre according to claim 4 or claim 5, **characterised by** a mass change of > 15 wt.%, preferably of > 30 wt.%, more preferably of > 65 wt.% by exposure to 90% relative humidity at 25 °C.

7. Polyamide fibre according to one of claims 4 to 6, **characterised by** a water retention value of > 30 wt.%, preferably of > 75 wt.%, more preferably of > 100 wt.%.

8. Polyamide fibre according to one of claims 4 to 7, **characterised in that** the ratio between the total diameter and the diameter of the core region is >1.

9. Textile, comprising a polyamide fibre according to one of claims 4 to 8.

10. Textile according to claim 9, **characterised in that** is woven, knitted or non-woven or it is a yarn or a rope.

11. Use of a polyamide fibre according to one of claims 4 to 8 or a textile according to claim 9 or claim 10 for storing and releasing liquids in pharmaceutical applications.

12. Use of a polyamide fibre according to one of claims 4 to 8 or a textile according to claim 9 or claim 10 for absorbing or anchoring chemical substances with additional functionalities onto the fibre surface.

13. Use of a polyamide fibre according to one of claims 4 to 8 or a textile according to claim 9 or claim 10 for absorbing dyes.

14. Use of a polyamide fibre according to one of claims 4 to 8 or a textile according to claim 9 or claim 10 in textile application requiring high moisture sorption capability like underwear.

15. Use of a polyamide fibre according to one of claims 4 to 8 or a textile according to claim 9 or claim 10 for enhancing the seam strength by adhesive and thermal bonding of textiles.

Fig. 1

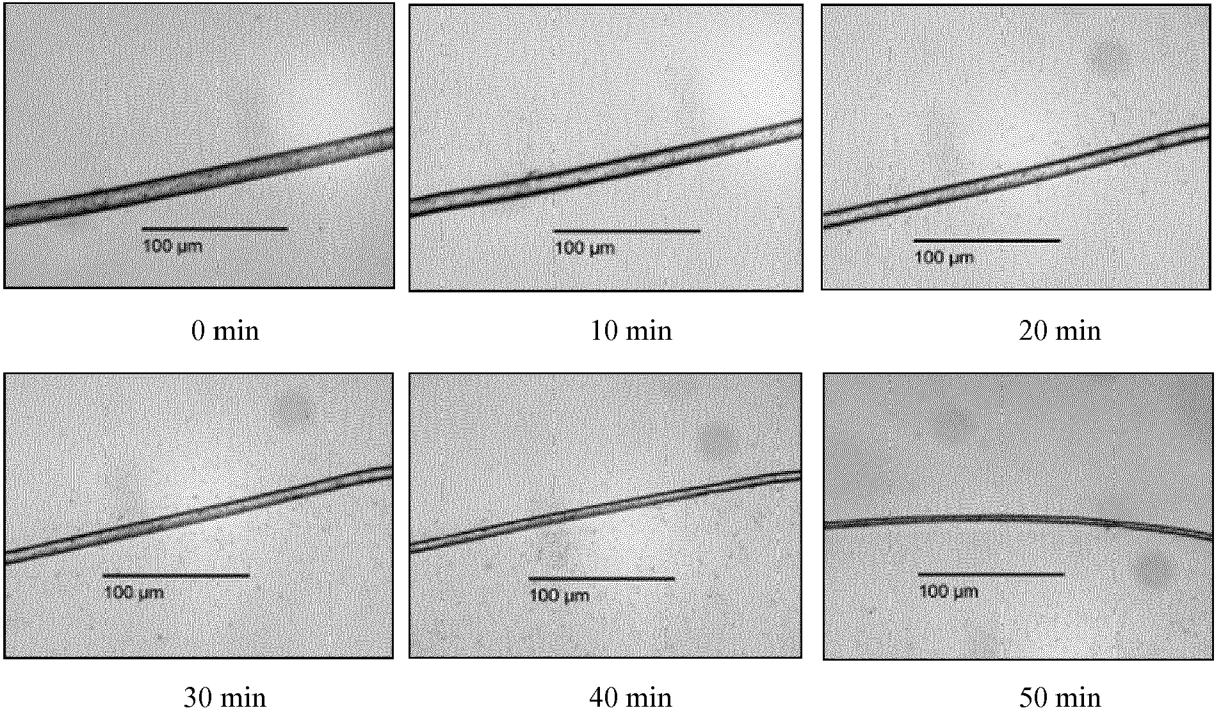

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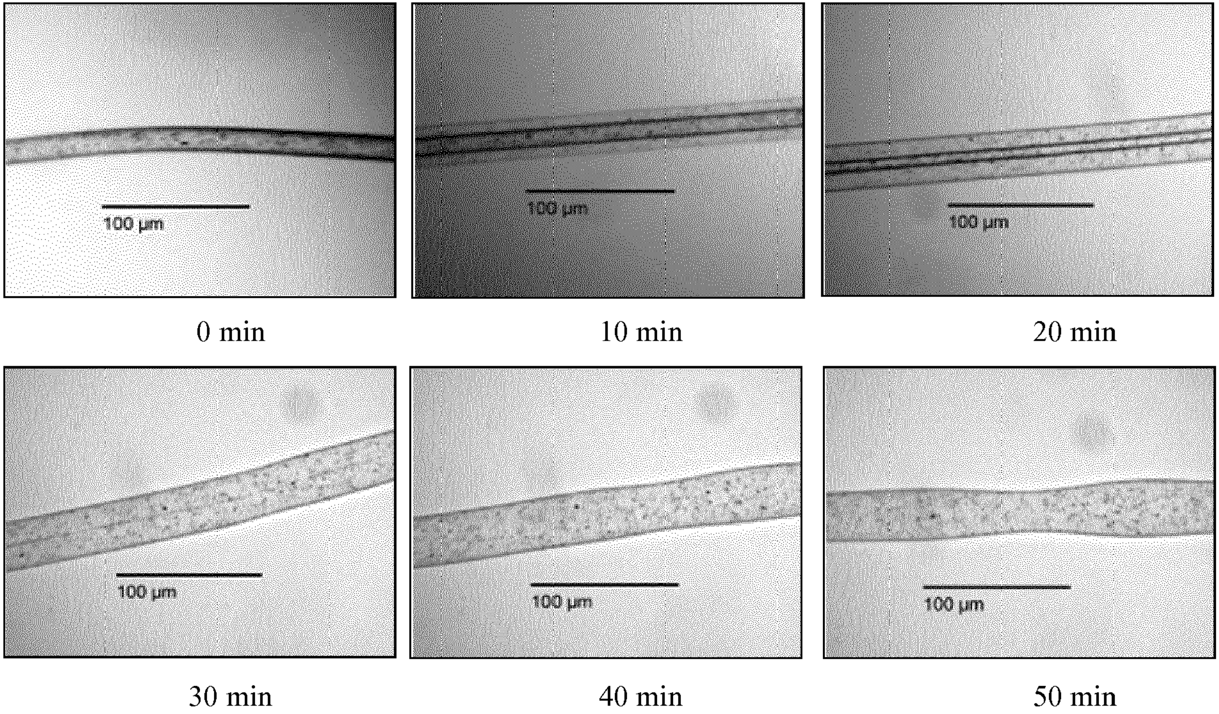
Fig. 2



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50 min

Fig. 3a

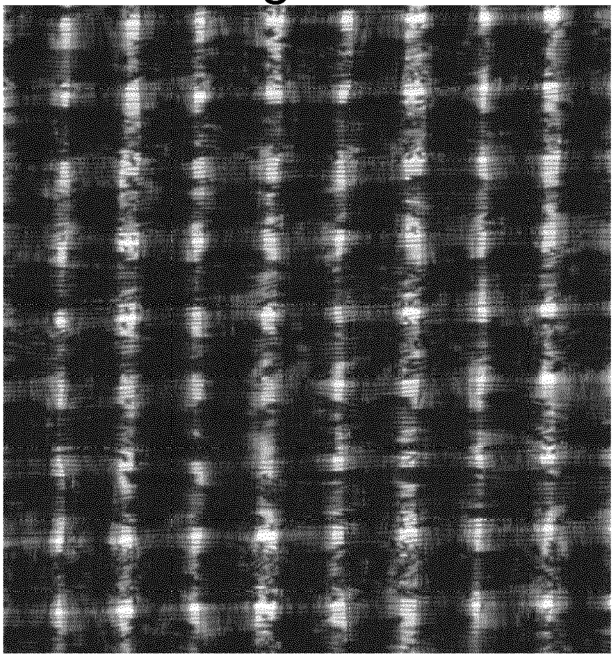

Fig. 3b

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EUROPEAN SEARCH REPORT

Application Number
EP 17 16 2290

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Place of search	Date of completion of the search	Examiner
The Hague	22 August 2017	Fiocco, Marco

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X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
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& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

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