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(54) HYDROPHOBIC COATING OF FIBRES, YARNS AND TEXTILES

(57) The present invention relates to a method for coating of elastic fibre or blended yarn comprising the coating of elastic fibre or blended yarn with an activated coating compound, yielding a covalently coated elastic fibre or covalently coated blended yarn, wherein the covalently coated elastic fibre or covalently coated blended yarn is characterised in that the coating has a thickness of 5 to 200 nm. The invention further relates to covalently coated elastic fibre or covalently coated blended yarn, a hydrophobically coated elastic textile comprising covalently coated elastic fibre or covalently coated blended yarn. The invention further relates to an apparatus for covalent coating of elastic fibre or blended yarn.

EP 4 528 019 A1

Description

Background

[0001] Elastic fibres made of an elastomer, typically containing a high amount of polyurethane, silicon or polymultiester, have a complex structure comprising soft elastomer and rigid polymer segments. Elastic fibres can be stretched to a multiple of their length providing a large surface for water to accumulate, resulting in long drying processes. Hydrophobic treatment of textiles is usually conducted using conventional wet chemical methods, wherein surface active compounds or crosslinking agents adhere to the textile fibre surfaces. However, such conventionally treated textiles have several disadvantages, wherein the hydrophobic coating does not sufficiently adhere to the elastic fibres within the textile and are thus only hydrophobic right after the hydrophobic treatment, but the hydrophobic effect decreases through wearing the textile and laundry processes. Additionally, such wet chemical methods produce an uneven hydrophobic coating, wherein filament surfaces lying on the inside are less hydrophobically coated than the outside surfaces of the filaments. As elastic fibres are often incorporated into a textile, wearing and washing of the textile results in a reorientation of the filaments inside the textile, exposing the non-coated parts of the elastic fibres and thus resulting in a decrease of the hydrophobic effect.

[0002] The state of the art discloses methods for hydrophobic coating of yarn and textiles.

[0003] The patent RU 2043438 C1 describes the principle of plasma treatment of fibres on one bobbin during rewinding onto a second bobbin. The patent EP 0695384 B1 discloses plasma coating of fibres and textile structures, e.g. for water repellence by means of chemical bonding of the plasma layer to the fibre surface. The patent EP 3697958 B1 discloses a method for preparing a textile with hydrophobically coated surface through plasma and wet chemical treatment.

[0004] Based on the above-mentioned state of the art, the objective of the present invention is to provide means and methods to prepare hydrophobically coated elastic fibres or yarns with improved hydrophobic properties, textiles made thereof as well as an apparatus for conducting hydrophobic treatment of elastic fibres or yarns. This objective is attained by the subject-matter of the independent claims of the present specification, with further advantageous embodiments described in the dependent claims, examples, figures and general description of this specification.

Summary of the Invention

[0005] A first aspect of the invention relates to a method for coating of elastic fibre or blended yarn comprising the coating of elastic fibre or blended yarn with an activated coating compound, yielding a covalently coated elastic fibre or covalently coated blended yarn, wherein the covalently coated elastic fibre or covalently coated blended yarn is characterised in that the coating has a thickness of 5 to 200 nm.

[0006] A second aspect of the invention relates to a covalently coated elastic fibre or covalently coated blended yarn, wherein the coating has a thickness of 5 to 200 nm.

[0007] A third aspect of the invention relates to a hydrophobic elastic textile comprising covalently coated elastic fibre or covalently coated blended yarn according to the second aspect of the invention, wherein the coating has a thickness of 5 to 200 nm.

[0008] A fourth aspect of the invention relates to an apparatus for covalent coating of elastic fibre or blended yarn comprising

a. a plasma chamber with at least one plasma zone,
b. at least one inner bobbin containing the elastic fibre or blended yarn,
c. an outer bobbin to wind up the elastic fibre or blended yarn,

wherein the at least one inner bobbin is localised inside the at least one plasma zone and the outer bobbin is localised outside the plasma chamber.

[0009] A fifth aspect of the invention relates to a covalently coated elastic fibre or covalently coated blended yarn, according to the first aspect of the invention, characterised in that the covalently coated elastic fibre or covalently coated blended yarn has hydrophobic properties.

Terms and definitions

[0010] For purposes of interpreting this specification, the following definitions will apply and whenever appropriate, terms used in the singular will also include the plural and vice versa. In the event that any definition set forth below conflicts with any document incorporated herein by reference, the definition set forth shall control.

[0011] The terms "comprising", "having", "containing", and "including", and other similar forms, and grammatical equivalents thereof, as used herein, are intended to be equivalent in meaning and to be open-ended in that an item or items following any one of these words is not meant to be an exhaustive listing of such item or items, or meant to be limited to only the listed item or items. For example, an article "comprising" components A, B, and C can consist of (i.e., contain only) components A, B, and C, or can contain not only components A, B, and C but also one or more other components. As such, it is intended and understood that "comprises" and similar forms thereof, and grammatical equivalents thereof, include disclosure of embodiments of "consisting essentially of" or "consisting of."

[0012] Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit, unless the context clearly dictates otherwise, between the upper and lower limit of that range and any other stated or intervening value in that stated range, is encompassed within the disclosure, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure.

[0013] Reference to "about" a value or parameter herein includes (and describes) variations that are directed to that value or parameter per se. For example, description referring to "about X" includes description of "X."

[0014] As used herein, including in the appended claims, the singular forms "a", "or" and "the" include plural referents unless the context clearly dictates otherwise.

[0015] "And/or" where used herein is to be taken as specific recitation of each of the two specified features or components with or without the other. Thus, the term "and/or" as used in a phrase such as "A and/or B" herein is intended to include "A and B," "A or B," "A" (alone), and "B" (alone). Likewise, the term "and/or" as used in a phrase such as "A, B, and/or C" is intended to encompass each of the following aspects: A, B, and C; A, B, or C; A or C; A or B; B or C; A and C; A and B; B and C; A (alone); B (alone); and C (alone).

[0016] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art (e.g. textile, yarn, etc). Standard techniques are used for textile manufacturing and wet chemical methods for hydrophobic coating (see generally, Lu Jing, Elastic Fibers, in: Handbook of Fibrous Materials, First Edition. Edited by Jinlian Hu, Bipin Kumar, and Jing Lu, 2020 Wiley-VCH Verlag GmbH & Co. KGaA; Waterproof and Water Repellent Textiles and Clothing, edited by John Williams, 2018 Elsevier Ltd).

[0017] The term *elastic fibre* in the context of the present specification relates to a fibre containing elastomer segments, a class of polymer fibre with a high elasticity and which can be stretched to a multiple of its length and return into its original state when the stretching force is omitted. Elastic fibre is commonly classified according to the elastic elongation, that is, high elastic fibre with elongation of 400 to 800 %, medium elastic fibre with elongation of 150 to 390 % and low elastic fibre with elongation of 20 to 150 %. Examples for elastic fibres are elastanes, based on polyurethane, silicones or polymultiester. Elastic fibre has a high elasticity, is shape-retaining, firm, tear-resistant and light.

[0018] The term *blended yarn* in the context of the present specification relates to yarn containing elastic fibres and non-elastic fibres, wherein elastic fibres are as defined herein and non-elastic fibres relate to polymer synthetic fibres which do not contain elastomer segments, including but not limited to polyethyleneterephthalate, polyamide, polypropylene, polyacryl and polylactid.

[0019] The term *activated coating compound* in the context of the present specification relates to a compound with hydrophobic properties, wherein a volatile precursor reacts and/or decomposes with or on a substrate, particularly the surface of the elastic fibre, yielding an activated coating compound by firmly (covalently) binding on the substrate.

[0020] The term *adjacent areas* in the context of the present specification relates to areas built when a covalently coated elastic fibre is stretched. The coating on the fibre surface is pulled apart when stretched and maintains contiguous areas, when the coiled elastomer segments of the elastic fibre are increasingly straightened.

[0021] The term *fluorocarbon* in the context of the present specification relates to chemical compounds with carbon-fluorine bonds, such as perfluorinated compounds containing further chemical elements and compounds consisting purely of fluorine and carbon atoms such as tetrafluoromethane, hexafluoropropene, octafluorocyclobutane.

[0022] The term *hydrofluorocarbon* in the context of the present specification relates to organic compounds that contain carbon, fluorine and hydrogen atoms, such as trifluoromethane, pentafluoropentane, tetrafluoroethane, and hexafluoropropane.

[0023] The term *hydrocarbon* in the context of the present specification relates to an organic compound consisting of hydrogen and carbon. Examples include are not limited to ethylene, acetylene, propene, butylene.

[0024] The term *covalently coated* in the context of the present specification relates to a strong chemical bond between the fibre surface and the activated coating compound, wherein the electrons participating in the covalent bond are distributed between the bonding partners, resulting in a stable bond. Covalently coated fibres are thus more stable against acting outer forces such as through abrasion or stretching.

[0025] Any patent document cited herein shall be deemed incorporated by reference herein in its entirety.

Detailed Description of the Invention

[0026] A first aspect of the invention, relates to a method for coating of elastic fibre or blended yarn comprising the coating of elastic fibre or blended yarn with an activated coating compound, yielding a covalently coated elastic fibre or covalently coated blended yarn, wherein the covalently coated elastic fibre or covalently coated blended yarn is characterised in that the coating has a thickness of 5 to 200 nm.

[0027] The elastomer segments of the elastic fibres can be straightened out resulting in the elastic properties of the fibres, while the rigid segments provide the fibre structure yielding solid strands. In the manufacturing process, prepolymers are drawn out to produce the solid strands that are bundled together to achieve long elastic fibres. Due to the natural stickiness of the elastic strands that adhere to one another, the elastic fibre has properties similar to a monofilament fibre. The sticky surface of the elastic fibre further requires the application of a finishing agent after the drawing process, typically a silicone oil. The finishing material is loosely applied and non-covalently bond to the elastic fibres. However, while the finishing material is hydrophobic, it gets easily spread or washed out, so that the elastic fibres lose their hydrophobicity over time.

[0028] The herein claimed method, however, is a method for directly coating the elastic fibre or a yarn comprising an elastic fibre, prior to incorporating them into a textile, wherein the coating is applied as a hydrophobic coating, the activated coating compound, which covalently binds onto the fibre or yarn yielding an adjustable coating of 5 to 200 nm thickness. The adjusted film thickness allows high adhesion of the activated coating compound at least on portions of the elastic fibre surface. When stretching the elastic fibre, covalently bound coating portions maintain contiguous areas that are pulled apart when the coiled elastomer segments are increasingly straightened. These coated portions forming adjacent areas are sufficient to provide hydrophobic properties to the elastic fibres.

[0029] Through the covalently bound coating throughout the entire fibre, the hydrophobic coating is more durable and less prone to be reduced in its effect due to wearing and washing and still allows further textile processing.

[0030] In certain embodiments, the method for coating of elastic fibre or blended yarn comprises the coating of elastic fibre or blended yarn with an activated coating compound, yielding a covalently coated elastic fibre or covalently coated blended yarn, wherein the covalently coated elastic fibre or covalently coated blended yarn is characterised in that the coating has a thickness of 10 to 100 nm.

[0031] In certain embodiments, the method for coating of elastic fibre or blended yarn comprises the coating of elastic fibre or blended yarn with an activated coating compound, yielding a covalently coated elastic fibre or covalently coated blended yarn, wherein the covalently coated elastic fibre or covalently coated blended yarn is characterised in that the coating has a thickness of 25 to 40 nm.

[0032] The film thickness of 25 to 40 nm is both, sufficiently thick to guarantee a highly hydrophobic surface, yet thin enough to allow unrestricted stretching and recoiling of the elastic fibres to avoid film failure under tensile and compressive stress.

[0033] In certain embodiments, the elastic fibre or blended yarn is washed prior to being coated with the activated coating compound, enabling covalent coating on the surface of the elastic fibre or blended yarn.

[0034] Washing of the elastic fibre or blended yarn prior to being coated at least partly removes the finishing agent applied to the elastic fibre, which is typically a silicon oil. In particular, the finishing agent, applied for handling the elastic fibres due to the natural stickiness of the elastic strands that adhere to one another is removed to an extent to uncover the fibre surface, while keeping the fibre structure, i.e. the sticking of the bundles, intact. Application of a coating can thus directly interact with the sticky fibre surface.

[0035] In certain embodiments, the method further comprises pre-stretching of the elastic fibre or blended yarn.

[0036] The elastic fibres are pre-stretched while applying the activated coating compound.

[0037] In certain embodiments, the elastic fibre or blended yarn is pre-stretched by at least 10%.

[0038] Pre-stretching of the elastic fibre or blended yarn by at least 10% allows for at least 50% surface coverage through the coating maintained during stretching and relaxing which provides a coated fibre or coated blended yarn with improved hydrophobic properties.

[0039] In certain embodiments, the elastic fibre or blended yarn is pre-stretched between 10% to 300%.

[0040] In certain embodiments, the elastic fibre or blended yarn is pre-stretched between 10% to 200%.

[0041] In certain embodiments, the elastic fibre or blended yarn is pre-stretched between 30% to 200%.

[0042] In certain embodiments, the method comprises winding the pre-stretched elastic fibre or pre-stretched blended yarn onto a bobbin, yielding winded elastic fibre or winded blended yarn.

[0043] In certain embodiments, the method comprises introducing the winded elastic fibre or winded blended yarn into a vacuum chamber.

[0044] In certain embodiments, the activated coating compound is applied onto washed elastic fibre or washed blended yarn using chemical vapor deposition.

[0045] In certain embodiments, the method comprises introducing the winded elastic fibre or winded blended yarn into a plasma chamber in such way that the outer fibres on the bobbin are facing the coating zone of the plasma.

[0046] In certain embodiments, the activated coating compound is applied onto washed elastic fibre or washed blended yarn using plasma polymerisation.

[0047] The activated coating compound is applied as a gaseous substance which is activated by the plasma to form a coating species at low temperatures. Through the energy input of the interaction with the plasma, the coating species become adhesive and are covalently bound onto the elastic fibre without altering the fibre bulk properties. The coating species show an improved infiltration through diffusion into the textile structure of the fibres coiled onto the bobbin, so that the fibres are coated not just in parts facing the plasma, but on the whole surface as well as partly on the inlying fibres.

[0048] In certain embodiments, the activated coating compound is applied to the elastic fibre or blended yarn by unwinding it from a bobbin at an unwinding speed of 10 to 1000 m/min.

[0049] Through simultaneous circulation of the bobbin and the unwinding of the fibres, the inlying fibres are gradually exposed and coated.

[0050] The activated coating compound can be applied to the elastic fibres or blended yarn on several bobbins placed in the plasma chamber simultaneously.

[0051] The thickness of the coating can be adjusted by the deposition rate of the activated coating compound and the residence time of the elastic fibre in a coating zone.

[0052] In certain embodiments, the activated coating compound is applied to the elastic fibre or blended yarn by unwinding it from a bobbin at an unwinding speed of 50 to 600 m/min.

[0053] In certain embodiments, the activated coating compound is applied to the elastic fibre or blended yarn by unwinding it from a bobbin at an unwinding speed of 100 to 600 m/min.

[0054] An unwinding speed of higher than 100 m/min increases the processual speed.

[0055] In certain embodiments, the activated coating compound is selected from the group consisting of organic silicon compounds, hydrofluorocarbons, fluorocarbons and hydrocarbons.

[0056] In certain embodiments, the activated coating compound is selected from the group consisting of organic silicon compounds and fluorocarbons.

[0057] In certain embodiments, the activated coating compound is selected from the group consisting of organic silicon compounds.

[0058] Organic silicon compounds are ecologically compatible.

[0059] In certain embodiments, the organic silicon compound is selected from a siloxane or silicone.

[0060] In certain embodiments, the organic silicon compound is a siloxane.

[0061] In certain embodiments, the organic silicon compound is a siloxane selected from the group consisting of hexamethyldisiloxane, tetramethyldisiloxane, 1,1,1,3,3,5,5,5-octamethyltrisiloxane, octamethylcyclotetrasiloxane.

[0062] In certain embodiments the organic silicon compound is a siloxane selected from the group consisting of hexamethyldisiloxane and octamethylcyclotetrasiloxane.

[0063] In certain embodiments, the activated coating compound is hexamethyldisiloxane.

[0064] In certain embodiments, the activated coating compound is gaseous.

[0065] In certain embodiments, the activated coating compound is mixed with argon gas.

[0066] In certain embodiments, coated elastic fibre or coated blended yarn is further spun to a textile.

[0067] In certain embodiments, the coated elastic fibre is spun to a textile.

[0068] The hydrophobically coated elastic fibre is incorporated into a textile using textile methods known to any skilled person, forming a yarn or a piece of textile.

[0069] In certain embodiments, the coated elastic fibre is spun to a textile and further coated with a hydrophobic compound.

[0070] The textile can undergo further wet chemical methods for further treatment with hydrophobic compounds. Textiles containing already hydrophobically coated elastic fibres according to the invention, have the advantage of being hydrophobically coated even on the inlying fibres and are thus, after additional wet chemical hydrophobic coating, coated throughout the entire textile having a long lasting hydrophobic effect. Insufficient adherence or a decreasing hydrophobic effect through appropriate washing and wearing the textile is avoided.

[0071] The textile has additionally better drying properties after storage in water and an improved wash resistance.

[0072] In certain embodiments, the elastic fibre is an elastane.

[0073] In certain embodiments, the elastic fibre is an elastane comprising polyurethane.

[0074] Elastane based on polyurethane has an increased colour fastness. This applies to elastic fibre used as such and blended yarn comprising elastic fibre.

[0075] A second aspect of the invention relates to a covalently coated elastic fibre or covalently coated blended yarn, wherein the coating has a thickness of 5 to 200 nm.

[0076] The adjusted film thickness allows high adhesion of the activated coating compound at least on portions of the elastic fibre surface during stretching and recoiling. Through the covalently bound coating throughout the entire fibre, the hydrophobic coating is more durable and less prone to be reduced in its effect due to wearing and washing and still allows further textile processing.

[0077] In certain embodiments, the covalently coated elastic fibre or covalently coated blended yarn has a coating with a thickness of 10 to 100 nm.

[0078] In certain embodiments, the covalently coated elastic fibre or covalently coated blended yarn has a coating with a thickness of 25 to 40 nm.

[0079] In certain embodiments, the covalently coated elastic fibre is an elastane.

[0080] In certain embodiments, the covalently coated elastic fibre is an elastane comprising polyurethane.

[0081] Elastane based on polyurethane has an increased colour fastness.

[0082] In certain embodiments, the covalently coated elastic fibre or covalently coated blended yarn is covalently coated in adjacent areas covering at least 50% of the fibre surface, when the covalently coated elastic fibre or covalently coated blended yarn is stretched to 300%, providing hydrophobic properties of the covalently coated elastic fibre.

[0083] In certain embodiments, the covalently coated elastic fibre or covalently coated blended yarn is covalently coated in adjacent areas covering at least 70% of the fibre surface, when the covalently coated elastic fibre or covalently coated blended yarn is stretched to 300%, providing hydrophobic properties of the covalently coated elastic fibre.

[0084] When stretching the elastic fibre, covalently bound coating portions maintain contiguous areas that are pulled apart when the coiled amorphous segments are increasingly straightened. These coated portions forming adjacent areas are sufficient to provide hydrophobic properties of the elastic fibres.

[0085] A third aspect of the invention relates to a hydrophobic elastic textile comprising covalently coated elastic fibre or covalently coated blended yarn according to the second aspect of the invention, wherein the coating has a thickness of 5 to 200 nm.

[0086] In certain embodiments, the hydrophobic elastic textile comprises covalently coated elastic fibre or covalently coated blended yarn according to the second aspect of the invention, wherein the coating has a thickness of 10 to 100 nm.

[0087] In certain embodiments, the hydrophobically elastic textile comprises covalently coated elastic fibre or covalently coated blended yarn according to the second aspect of the invention, wherein the coating has a thickness of 25 to 40 nm.

[0088] In certain embodiments, the hydrophobic elastic textile is further coated with a hydrophobic compound.

[0089] The textile can undergo further wet chemical methods for further treatment with hydrophobic compounds. Textiles containing already hydrophobically coated elastic fibres have the advantage of being hydrophobically coated even on the inlying fibres and thus, after additional wet chemical hydrophobic coating coated throughout the entire textile, have a long lasting hydrophobic effect. Insufficient adherence or a decreasing hydrophobic effect through washing and wearing the textile is avoided.

[0090] The textile has additionally better drying properties after storage in water and an improved wash resistance.

[0091] In certain embodiments, the hydrophobic elastic textile comprises covalently coated elastic fibre according to the second aspect of the invention and non-elastic fibres.

[0092] In certain embodiments, the non-elastic fibres are hydrophobically, covalently coated prior to being spun into the textile.

[0093] The non-elastic fibres are covalently coated according to the method of the first aspect of the invention.

[0094] The textile comprising covalently coated elastic fibres and covalently coated non-elastic fibres has improved hydrophobic properties.

[0095] In certain embodiments, the hydrophobic elastic textile comprises covalently coated elastic fibre according to the second aspect of the invention and non-elastic fibres, wherein the non-elastic fibres are hydrophobically, covalently coated prior to being spun into the textile and wherein the hydrophobic elastic textile is further coated with a hydrophobic compound.

[0096] Additional hydrophobic treatment of the hydrophobic elastic textile using wet chemical methods can improve the grip or the permeability of the textile.

[0097] In certain embodiments, the hydrophobic elastic textile comprises covalently coated blended yarn comprising elastic fibre.

[0098] A fourth aspect of the invention relates to an apparatus for covalent coating of elastic fibre or blended yarn comprising

d. a plasma chamber with at least one plasma zone,
e. at least one inner bobbin containing the elastic fibre or blended yarn,
f. at least one outer bobbin to wind up the elastic fibre or blended yarn,

wherein the at least one inner bobbin is localised inside the at least one plasma zone and the outer bobbin is localised outside the plasma chamber.

[0099] The apparatus allows for an increased processual rate as an increased amount of fibre or yarn can be introduced into a plasma zone by winding on at least one inner bobbin.

[0100] In certain embodiments, the plasma chamber with at least one plasma zone is a plasma chamber with at least one inductively coupled plasma zone.

[0101] In certain embodiments, the apparatus comprises a source for a coating compound to be uniformly introduced into the plasma zone.

[0102] In certain embodiments, the apparatus comprises an argon source used as carrier gas for the coating compound.

[0103] In certain embodiments, the apparatus for covalent coating of elastic fibre or blended yarn comprising

a. a plasma chamber with one plasma zone,
b. one inner bobbin containing the elastic fibre or blended yarn,
c. an outer bobbin to wind up the elastic fibre or blended yarn,

wherein the inner bobbin is localised inside the plasma zone and the outer bobbin is localised outside the plasma chamber.

[0104] In certain embodiments, the apparatus for covalent coating of elastic fibre or blended yarn comprising

a. a plasma chamber with two plasma zones,
b. six inner bobbins containing the elastic fibre or blended yarn,
c. up to six outer bobbins to wind up the elastic fibre or blended yarn,

wherein the six inner bobbins are localised inside the plasma zone and the up to six outer bobbins are localised outside the plasma chamber.

[0105] The throughput using an apparatus comprising six inner bobbins is increased six times compared to an apparatus comprising one inner bobbin.

[0106] In certain embodiments, the two plasma zones are located at opposite ends of the plasma chamber.

[0107] In certain embodiments, three of the six bobbins are located in one of the two plasma zones and three of the six bobbins are located in the other of the two plasma zones on the opposite side of the plasma chamber.

[0108] In certain embodiments, the apparatus has two sources of the coating compound in case the apparatus comprises two plasma zones.

[0109] The invention is further illustrated by the following examples and figures, from which further embodiments and advantages can be drawn. These examples are meant to illustrate the invention but not to limit its scope.

[0110] A fifth aspect of the invention relates to a covalently coated elastic fibre or covalently coated blended yarn, according to the first aspect of the invention, characterised in that the covalently coated elastic fibre or covalently coated blended yarn has hydrophobic properties.

[0111] A covalently coated elastic fibre or blended yarn has increased hydrophobic properties and faster drying properties than non-covalently coated elastic fibre or non-covalently coated blended yarn.

Description of the Figures

[0112]

Fig. 1 shows a covalently coated elastic fibre which was coated in a 10% pre-stretched state in a) its relaxed state showing no adjacent areas and a continuous coating layer; b) its stressed state at 300% stretch showing adjacent areas of on average 2 μm wide portions of the hydrophobic coating transverse to the fibre direction covering around 50% of the fibre surface. SEM images are 60 μm wide.

Fig. 2 shows a covalently coated elastic fibre which was coated in a 30% pre-stretched state in a) its relaxed state showing a slight corrugation and 100% coverage of the fibre surface with the hydrophobic coating; b) its stressed state at 300% stretch showing adjacent areas of on average 2 μm wide portions of the hydrophobic coating transverse to the fibre direction covering around 60% of the fibre surface. SEM pictures are a) 120 μm and b) 60 μm wide.

Fig. 3 shows a covalently coated elastic fibre which was coated in a 100% prestretched state in a) its relaxed state showing slightly corrugated adjacent areas of the hydrophobic coating interrupted along the fibre direction covering still almost 100% of the fibre surface; b) its prestretched state of 100% during the coating process showing a continuous layer of hydrophobic coating; c) its stressed state at 300% stretch showing adjacent areas of on average 5 μm wide portions of the hydrophobic coating transverse to the fibre direction covering around 70% of the fibre surface. SEM pictures are a) 50 μm, b) 60 μm and c) 120 μm wide.

Fig. 4 shows a covalently coated elastic fibre which was coated in a 200% prestretched state in a) its relaxed state showing corrugated adjacent areas of the hydrophobic coating distinctly interrupted along the fibre direction covering 70% of the fibre surface; b) its stressed state at 300% stretch showing adjacent areas of on average 4 μm wide portions of the hydrophobic coating transverse to the fibre direction covering 80-90% of the fibre surface. SEM pictures are 130 μm wide.

Fig. 5 shows a plot of the deposition rate normalized to the gas flow rate of the precursor hexamethyldisiloxane (HMDSO) vs. the energy input, given by power input per HMDSO flow rate for an inductively coupled plasma (ICP) at a pressure of 3 Pa with argon as carrier gas. The optimum deposition rate and hydrophobic properties are observed at the highest point of the linearly increasing deposition rate according to an apparent threshold energy, E_{th}, here 60 nm/min and 103° water contact angle on a flat reference sample. Lower energy input yield the same hydrophobic properties at reduced deposition rate, while higher energy input results in reduced hydrophobic properties.

Fig. 6 shows the covalently coated fibre of a textile made of such fibres which were further wrapped with polyamide fibres into a blended covered yarn. The covered yarn was used to produce the textile and said textile was further hydrophobically coated using wet chemical methods. Fig. 6 shows that the covalent coating of the covalently coated elastic fibres is maintained throughout the textile fabrication resulting in a textile with equally hydrophobic properties as the covalently coated elastic fibres. SEM image is 30 μm wide.

Fig. 7 shows the covalently coated elastic fibre of a covered yarn, wherein the covered yarn is a blended yarn consisting of covalently hydrophobic coated elastic fibre and covalently hydrophobic coated polyethylene terephthalate (PET) fibre. Fig. 7 shows that the covalent coating of the covalently coated elastic fibres is maintained throughout the textile fabrication resulting in a textile with equally hydrophobic properties as the covalently coated elastic fibres. a) shows the elastic fibres and PET fibres at low resolution; b) shows the elastic fibres at higher resolution. SEM images are a) 1.2 mm and b) 20 μm wide.

Fig. 8 shows the drying properties of different hydrophobically treated textiles after 20 min immersion in water. A dendrimer (siloxane-containing) finish and a fluorocarbon (C6) finish applied to a PA/EL (15%) fabric ('orig') is compared to the same fabric containing covalently coated ('CC') elastic fibre with subsequent hydrophobic finish and covalently coated blended covered yarn (PET/EL (15%)) without further hydrophobic finish according to the invention. For comparison, the best performance of a hydrocarbon finish (paraffin) is added. a) shows the drying properties regarding the weight gained by water intake before washing, indicating good drying properties except for the hydrocarbon finish; b) shows the drying properties of the same fabrics after five washing cycles (each 45 min, 50°C, 150 ml water + 0.25 g detergent, with steel balls), indicating that only the covalently coated (CC) elastic fibres with fluorocarbon finish and the covalently coated blended covered yarn (PET/EL) maintain their good drying properties.

Examples

Example 1: Production of covalently coated elastic fibre

[0113] An elastic fibre made of elastane (EL 78 dtex) is first cleaned in a roll-to-roll process to partly remove the finishing agent and to uncover the fibre surface. The slightly pre-stretched fibres provided on a bobbin are winded through an ultrasonic cleaning bath with following parameters:

Length of the fibre in the bath: 4.5 m

Fiber-in velocity: 30-35 m/min

Fiber-out velocity: 55-65 m/min

Wash solution: 1 mg Rucogen ESC per liter water (70°C)

[0114] By leaving the cleaning bath, the fibre is immediately dried with an air dryer at 100°C before winding up on a second bobbin.

[0115] Upon winding, the fibres are stretched to 100%. The fibre is re-winded to reach a defined pre-stretching of 50%, using 60 m/min for the winder and 30 m/min for the take-up reel. Thereby, the inner bobbin is provided containing the fibre for the coating process.

[0116] For the low pressure plasma coating process, the bobbin carrying the pre-stretched, cleaned and uncoated fibre is centered in front of an inductively-coupled plasma (ICP) source with 80 mm distance. By turning the inner bobbin the outermost fibre layers on the bobbin are exposed to the plasma zone, while the fibre is steadily removed from the bobbin, guided through a differentially pumped vacuum tube and winded up at ambient conditions on a second, outer bobbin.

Coating process parameters:

[0117]

Velocity of winding in the plasma chamber (unwinding): 120 m/min

Plasma excitation frequency of ICP source: RF (13. 56 MHz)

RF power: 200 W

Pressure: 3 Pa

Gas flow rates: HMDSO 4 sccm, argon 46 sccm

Deposition rate on turning inner bobbin: 30 nm/min

Fibre length exposed to plasma zone: 140 m

[0118] According to these settings, a nominal coating thickness of 35 nm is observed on the pre-stretched elastic fibre. Such covalently coated hydrophobic elastic fibres are then used for further textile processes.

Example 2: Production of blended yarn

[0119] An elastic fibre made of elastane (EL 78 dtex) is covalently coated according to Example 1. A second, non-elastic uncoated yarn made of polyamide 6.6 (PA 78 dtex x2) is used to cover the covalently coated hydrophobic elastic fibre made of elastane (EL 78 dtex) to produce a blended yarn (PA/EL (15%)).

Example 3: Production of covalently coated blended yarn

[0120] A blended yarn (PET/EL (15%)) is produced similar to Example 2 by using an uncoated elastic fibre made of elastane (EL 78 dtex) and an uncoated non-elastic yarn made of polyethylene terephthalate (PET 78 dtex x2). The blended yarn is first cleaned in a roll-to-roll process according to Example 1.

[0121] The blended yarn is winded on a bobbin applying a pre-stretching of 200% with respect to the elastic fibre. The bobbin is centered in front of an inductively-coupled plasma (ICP) source with 80 mm distance for the low pressure plasma coating process. By turning the inner bobbin the outermost fibre layers on the bobbin are exposed to the plasma zone, while the yarn is steadily removed from the bobbin, guided through a differentially pumped vacuum tube and winded up at ambient conditions on a second, outer bobbin.

Coating process parameters:

[0122]

Velocity of winding in the plasma chamber (unwinding): 30 m/min

Plasma excitation frequency of ICP source: RF (13. 56 MHz)

RF power: 200 W

Pressure: 3 Pa

Gas flow rates: HMDSO 6 sccm, argon 44 sccm

Deposition rate on turning inner bobbin: 40 nm/min

Fibre length exposed to plasma zone: 3x 30 m

[0123] According to these settings, a nominal coating thickness of 40 nm of a hydrophobic coating is observed on the blended yarn.

Example 4: Production of covalently coated blended covered yarn

[0124] An elastic fibre made of elastane (EL 78 dtex) is covalently coated according to example 1. Likewise, a second, non-elastic yarn made of polyethylene terephthalate (PET 78 dtex x2) is covalently coated. The yarn is provided as a pre-cleaned yarn, thus not further cleaning is applied.

[0125] The non-elastic, uncoated yarn is winded without pre-stretching on the inner bobbin for the low pressure plasma coating process, centered in front of an inductively-coupled plasma (ICP) source with 80 mm distance. By turning the inner bobbin the outermost fibre layers on the bobbin are exposed to the plasma zone, while the yarn is steadily removed from the bobbin, guided through a differentially pumped vacuum tube and winded up at ambient conditions on a second, outer bobbin.

Coating process parameters:

[0126]

Velocity of winding in the plasma chamber (unwinding): 120 m/min

Plasma excitation frequency of ICP source: RF (13. 56 MHz)

RF power: 200 W

Pressure: 3 Pa

Gas flow rates: HMDSO 6 sccm, argon 44 sccm

Deposition rate on turning inner bobbin: 40 nm/min

Fibre length exposed to plasma zone: 2x 75 m

[0127] According to these settings, a nominal coating thickness of 25 nm is observed on the non-elastic yarn. Similar to Example 2, such covalently coated hydrophobic non-elastic yarn is then used to cover the covalently coated hydrophobic elastic fibre made of elastane (EL 78 dtex) to produce a covalently coated blended covered yarn (PET/EL (15%)).

Characterization: film thickness on elastic fibre

[0128] The following two methods are used to determine the coating thickness.

A) Film thickness by deposition rate determination

[0129] The deposition rate is determined on the turning bobbin by placing a masked silicon wafer sample at the position of the fibre and measuring the film thickness after deposition along the edge of the unmasked sample by profilometry. The film thickness on the fiber is then calculated regarding the fibre length exposed to the plasma zone and the velocity of winding.

B) Gravimetric film thickness determination

[0130] By measuring the fibre weight before and after the coating process, the mass of the deposited coating can be obtained. With the density and the dimension of the fibre, the film thickness can then be calculated.

[0131] Both methods were found to agree well.

Characterization: SEM, drying time, washing

[0132] Scanning Electron Microscopy (SEM) is used to investigate the morphology of the samples. In SEM an accelerated and focused electron beam is scanned across the sample surface in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography. A Hitachi S-4800 microscope was used with the parameters of 2 kV acceleration voltage, 8 mm work distance and 10 μA emission current. The samples were cut to appropriate sizes and put onto a sample holder (attached with double-sided carbon adhesive tape). Stretched fibers were fixed at its elongation using strong gluing tape. All samples were made conductive (necessary for proper measurements) via sputtering of a 10 nm thin Au/Pd layer onto the samples.

[0133] For investigating the drying properties, fabric samples were cut to ca. 50 x 50 mm^2 pieces and stored in distillated water with a constant temperature of 23.1 degree Celsius. Thereby, the samples were loosely fixed to the bottom of the glass beaker containing the water with aluminum plates of 100 grams weight each. After 20 min. the samples were taken out and let drip down residual water droplets by holding the fabric in a vertical state. Afterwards, the weight of the fabric was measured in fixed time intervals (namely after 0.5, 1, 2, 3, 4, 5, 10, 15, 20, 30, and 60 min), thereby storing/drying the sample in an environment of fixed temperature of 23.1 degree Celsius and fixed relative humidity of 50%.

[0134] Washing trials were performed for a duration of 45 minutes at a temperature of 50 degree Celsius using 150 ml of water and 0.25 g of detergent (ECE-98). To simulate five typical washing cycles, steel balls with a diameter of 4 mm were applied to the washing container.

Cited prior art documents:

[0135]

1. RU 2043438 C1, 1992

2. EP 0695384 B1, 1993

3. EP 3697958 B1, 2017

[0136] All scientific publications and patent documents cited in the present specification are incorporated by reference herein.

Claims

1. A method for coating of elastic fibre or blended yarn comprising the coating of elastic fibre or blended yarn with an activated coating compound, yielding a covalently coated elastic fibre or covalently coated blended yarn, wherein the covalently coated elastic fibre or covalently coated blended yarn is **characterised in that** the coating has a thickness of 5 to 200 nm, particularly of 10 to 100 nm, more particularly of 25 to 40 nm.

2. The method according to claim 1, wherein the elastic fibre or blended yarn is washed prior to being coated with the activated coating compound, enabling covalent coating on the surface of the elastic fibre or blended yarn.

3. The method according to any of the preceding claims, wherein the activated coating compound is applied onto washed elastic fibre or washed blended yarn using chemical vapor deposition.

4. The method according to any of the preceding claims, wherein the activated coating compound is applied onto washed elastic fibre or washed blended yarn using plasma polymerisation.

5. The method according to any of the preceding claims, wherein the method further comprises pre-stretching of the elastic fibre or blended yarn.

6. The method according to claim 5, wherein the elastic fibre or blended yarn is pre-stretched by at least 10%, particularly wherein the elastic fibre or blended yarn is pre-stretched between 10% to 300%, more particularly wherein the elastic fibre or blended yarn is pre-stretched between 30% to 200%.

7. The method according to any of the preceding claims, wherein the activated coating compound is applied to the elastic fibre or blended yarn by unwinding it from a bobbin at an unwinding speed of 10 to 1000 m/min, particularly wherein the activated coating compound is applied to the elastic fibre or blended yarn by unwinding it from a bobbin at an unwinding speed of 50 to 600 m/min.

8. The method according to any of the preceding claims, wherein the activated coating compound is selected from the group consisting of organic silicon compounds, hydrofluorocarbons, fluorocarbons and hydrocarbons, particularly wherein the activated coating compound is selected from the group consisting of organic silicon compounds and fluorocarbons, more particularly wherein the activated coating compound is selected from the group consisting of organic silicon compounds.

9. The method according to claim 8, wherein the organic silicon compound is a siloxane particularly a siloxane selected from the group consisting of hexamethyldisiloxane, tetramethyldisiloxane, 1,1,1,3,3,5,5,5-octamethyltrisiloxane, octamethylcyclotetrasiloxane .

10. The method according to any of the preceding claims, wherein coated elastic fibre or coated blended yarn is further spun to a textile.

11. A covalently coated elastic fibre or covalently coated blended yarn, wherein the coating has a thickness of 5 to 200 nm, particularly of 10 to 100 nm, more particularly of 25 to 40 nm.

12. The covalently coated elastic fibre or covalently coated blended yarn according to claim 11, wherein the covalently coated elastic fibre is covalently coated in adjacent areas covering at least 50% of fibre surface, when the covalently coated elastic fibre or covalently coated blended yarn is stretched to

300%, providing hydrophobic properties of the covalently coated elastic fibre or covalently coated blended yarn, particularly wherein the covalently coated elastic fibre is covalently coated in adjacent areas covering at least 70% of the fibre surface, when the covalently coated elastic fibre or covalently coated blended yarn is stretched to 300%.

13. A covalently coated elastic fibre or covalently coated blended yarn, according to the method of claims 1 to 10, **characterised in that** the covalently coated elastic fibre or covalently coated blended yarn has hydrophobic properties.

14. A hydrophobic elastic textile comprising covalently coated elastic fibre or covalently coated blended yarn according to claim 11 and 12, wherein the coating has a thickness of 5 to 200 nm, particularly of 10 to 100 nm, more particularly of 25 to 40 nm.

15. An apparatus for covalent coating of elastic fibre or blended yarn comprising

a. a plasma chamber with at least one plasma zone, particularly a plasma chamber with at least one inductively couple plasma zone,
b. at least one inner bobbin containing the elastic fibre or blended yarn,
c. at least one outer bobbin to wind up the elastic fibre or blended yarn,

wherein the at least one inner bobbin is localised inside the at least one plasma zone and the outer bobbin is localised outside the plasma chamber.

Fig. 1

a)

b)

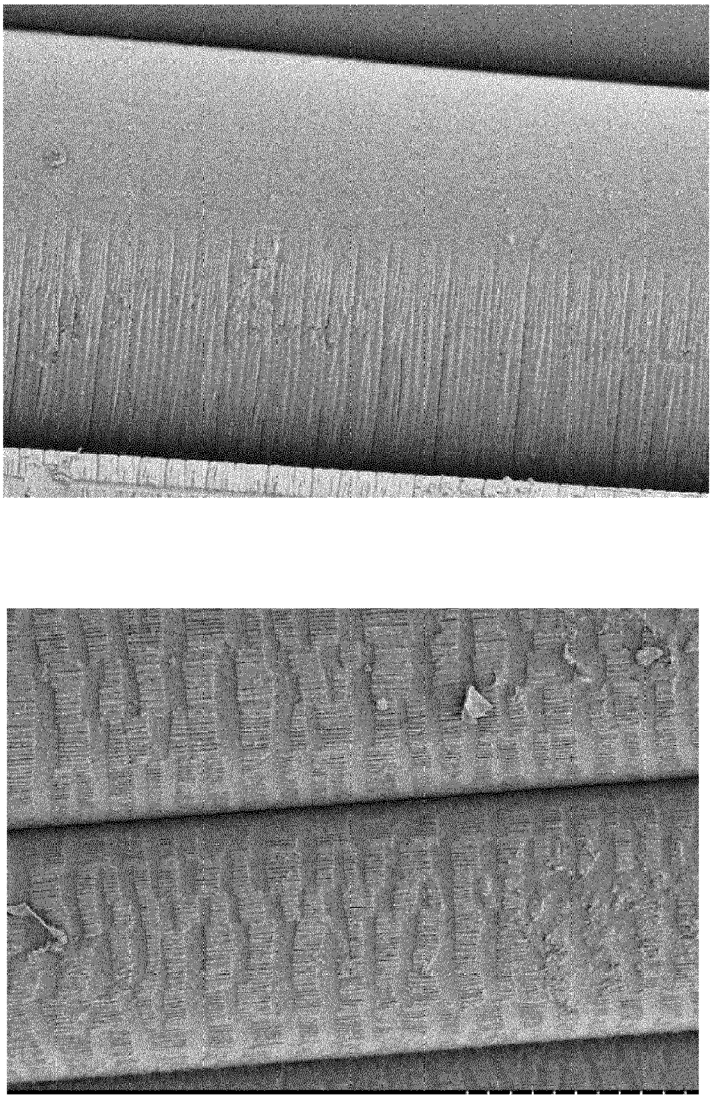
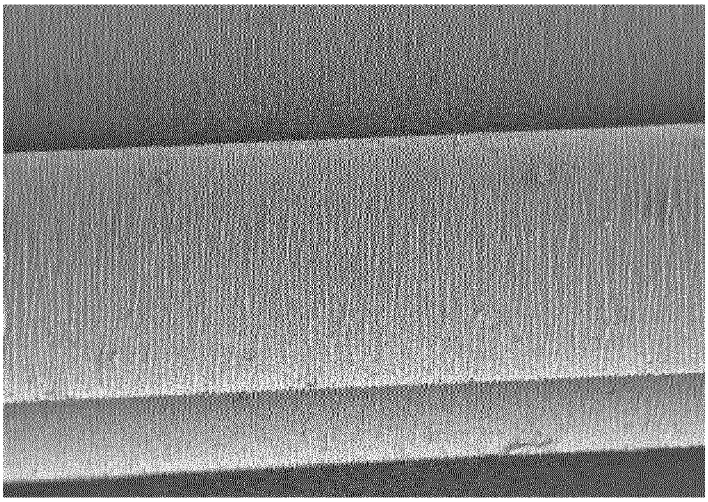


Fig. 2

a)



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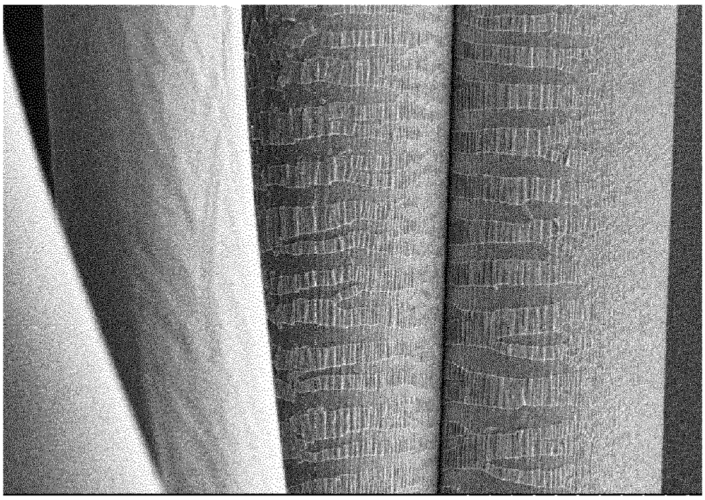


Fig. 3

a)

b)

c)

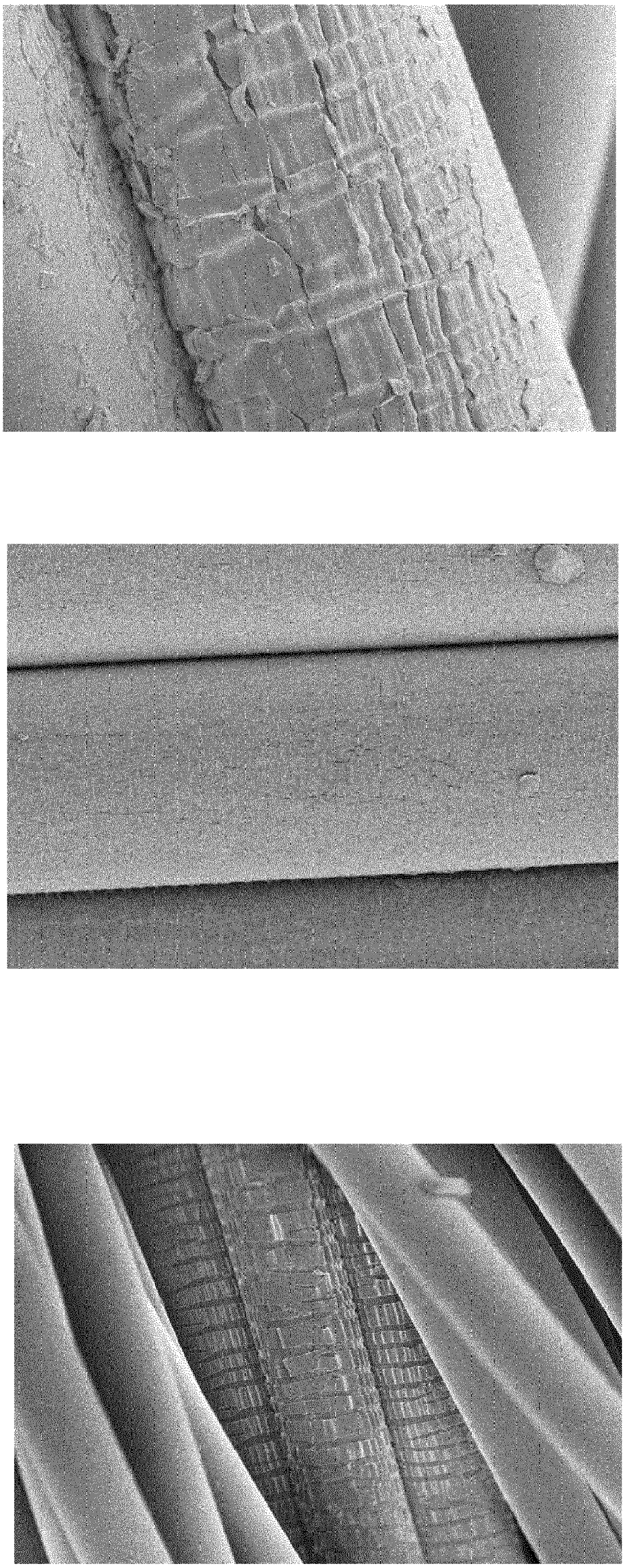
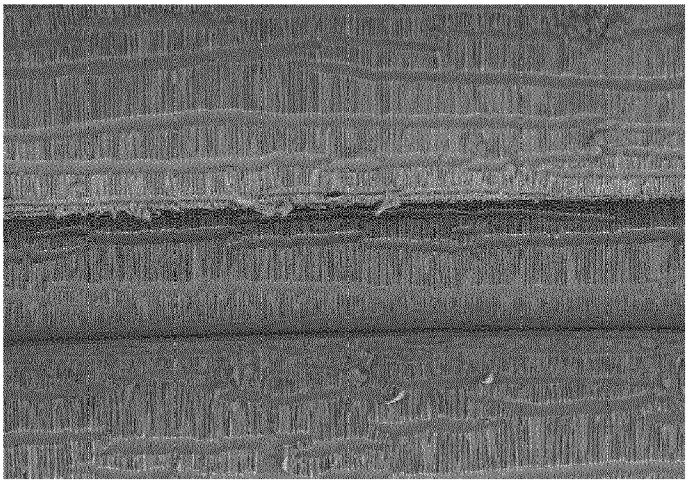


Fig. 4

a)



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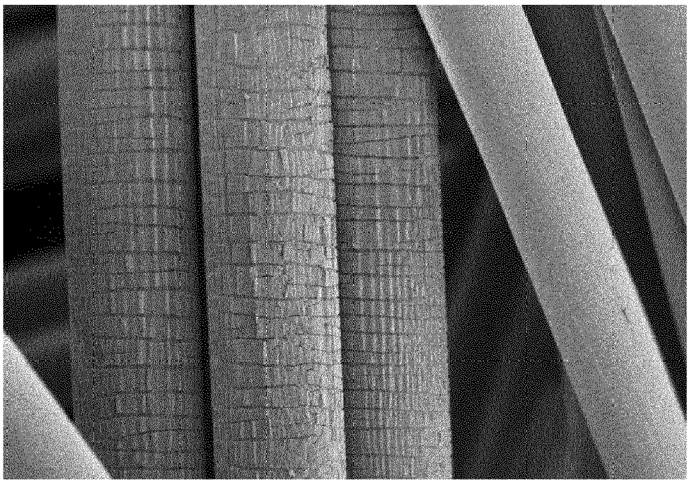
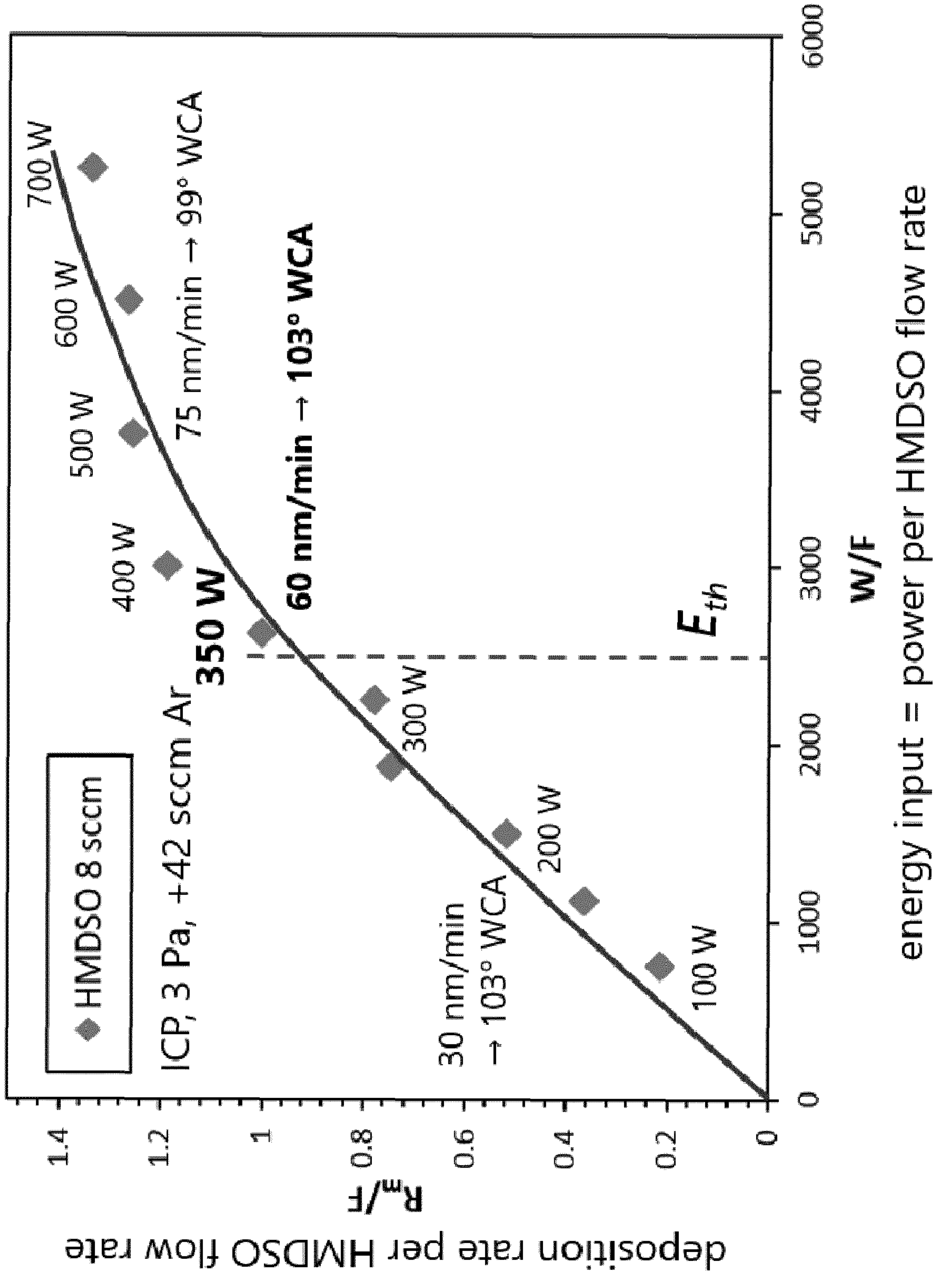


Fig. 5



HMDSO 8 sccm
ICP, 3 Pa, +42 sccm Ar
30 nm/min
→ 103° WCA
60 nm/min → 103° WCA
75 nm/min → 99° WCA
100 W
200 W
300 W
350 W
400 W
500 W
600 W
700 W
E_{th}
W/F
energy input = power per HMDSO flow rate
R_m/F
deposition rate per HMDSO flow rate
0
0.2
0.4
0.6
0.8
1
1.2
1.4
0
1000
2000
3000
4000
5000
6000

Fig. 6

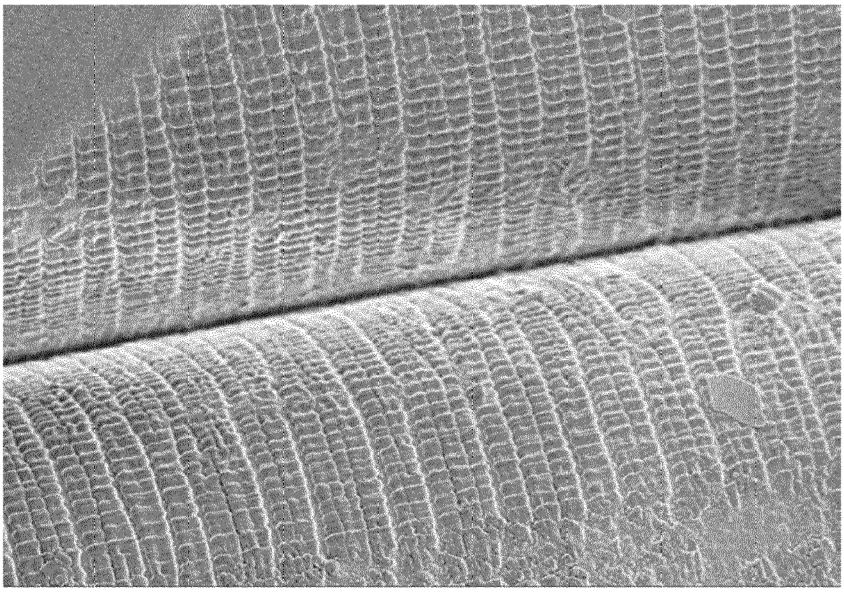
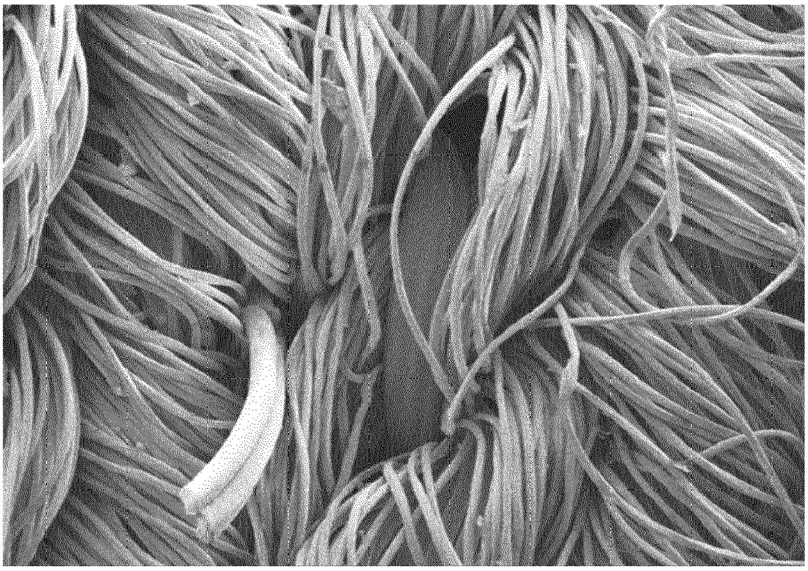


Fig. 7

a)



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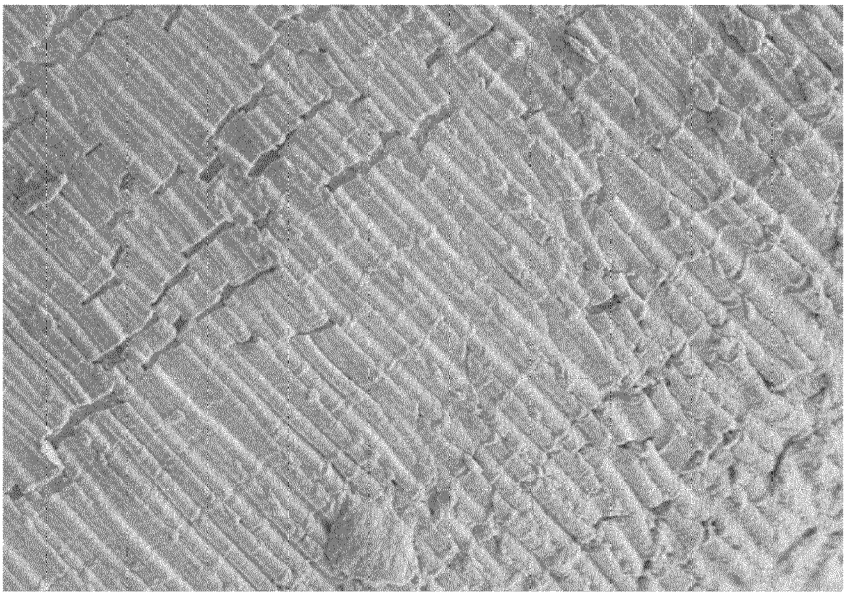
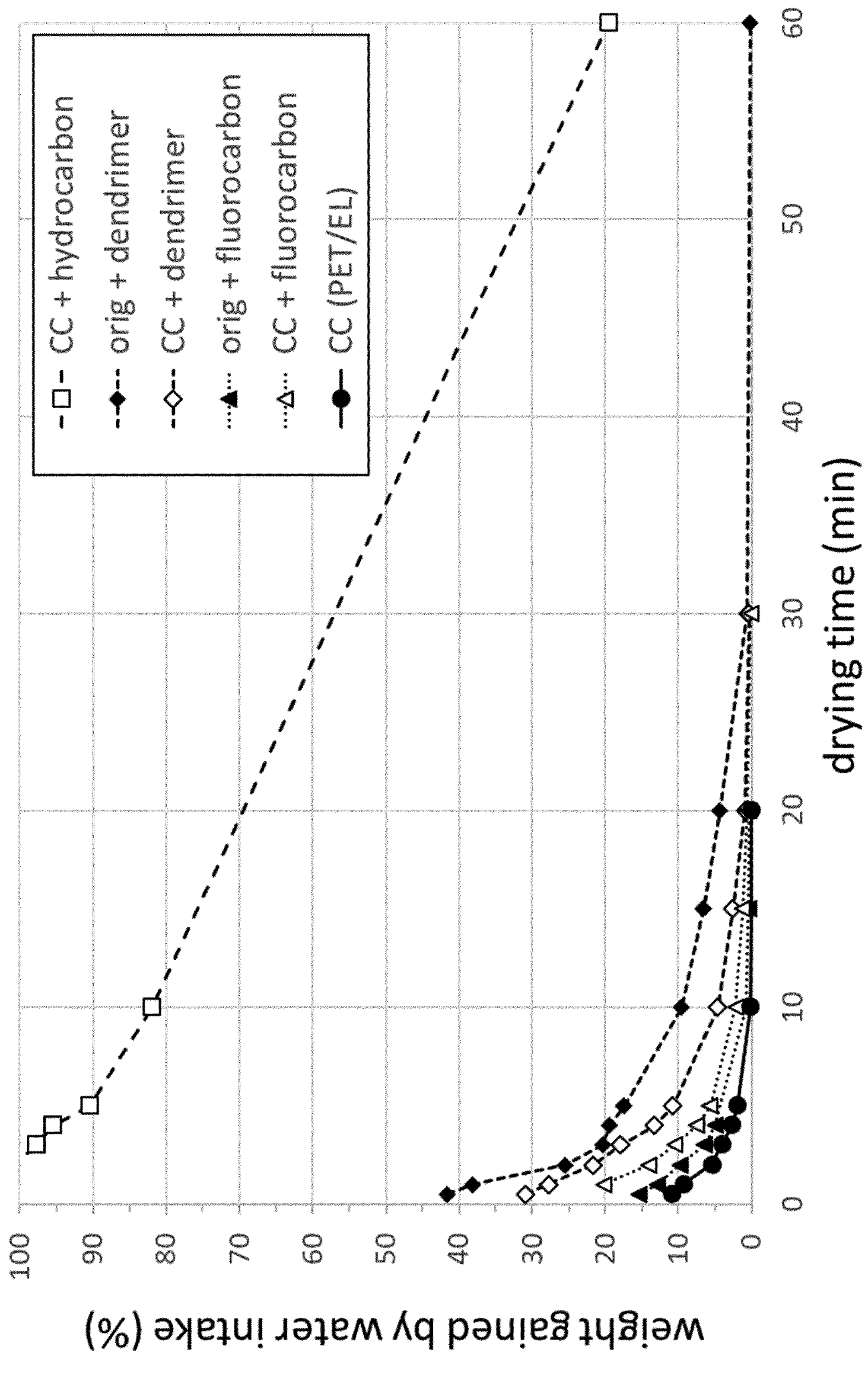
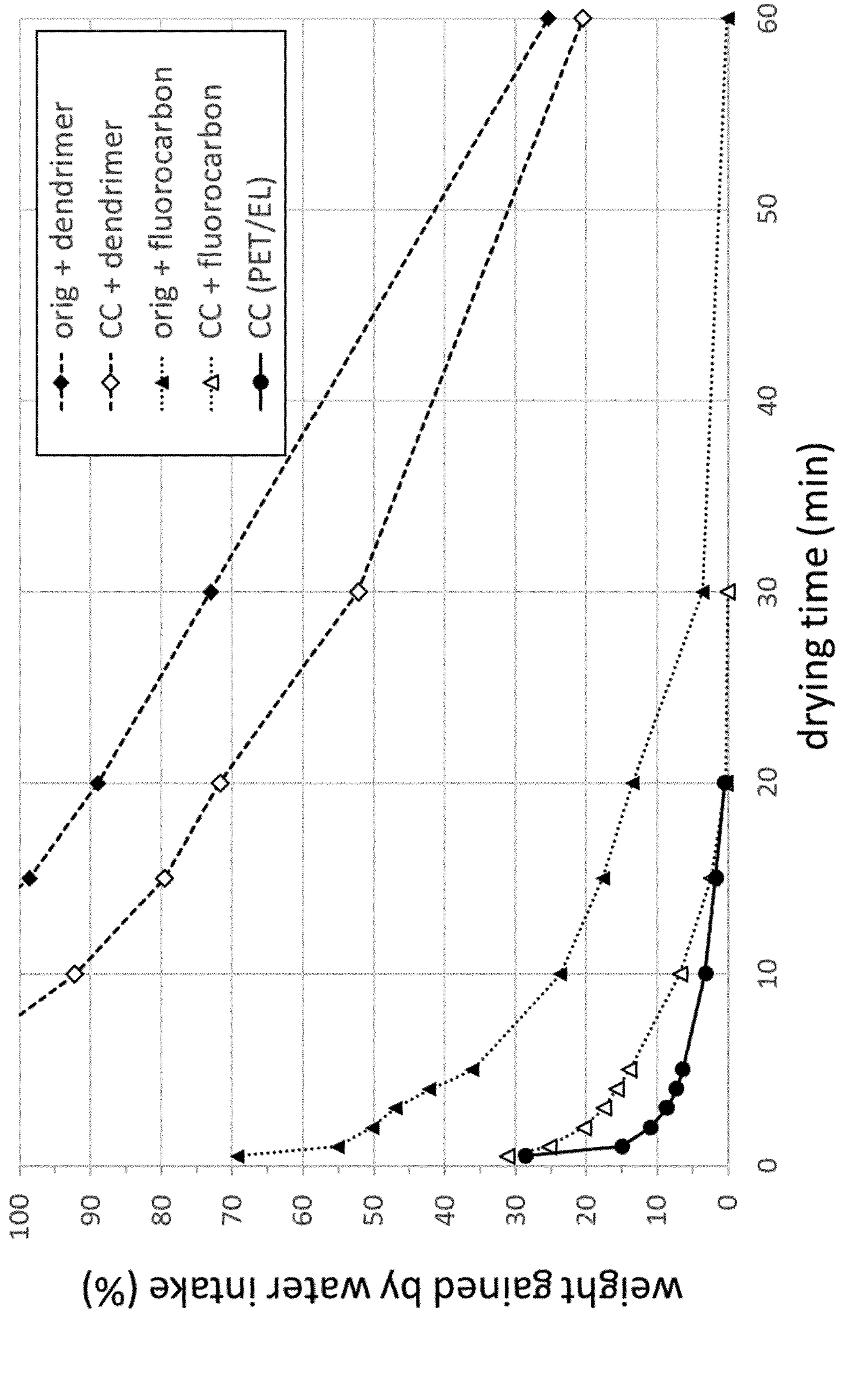


Fig. 8

a)


CC + hydrocarbon
orig + dendrimer
CC + dendrimer
orig + fluorocarbon
CC + fluorocarbon
CC (PET/EL)
drying time (min)
weight gained by water intake (%)
0
10
20
30
40
50
60
70
80
90
100

b)


orig + dendrimer
CC + dendrimer
orig + fluorocarbon
CC + fluorocarbon
CC (PET/EL)
weight gained by water intake (%)
drying time (min)
0
10
20
30
40
50
60
70
80
90
100
0
10
20
30
40
50
60

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EUROPEAN SEARCH REPORT

Application Number
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			D06M

3

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	2 May 2024	Queste, Sébastien

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