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A Simple, One-Step Approach to Durable and Robust Superhydrophobic Textiles**

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Superhydrophobic textile fabrics are prepared by a simple, one-step gas phase coating procedure by which a layer of polymethylsilsesquioxane nanofilaments is grown onto the individual textile fibers. A total of 11 textile fabrics made from natural and man made fibers are successfully coated and their superhydrophobic properties evaluated by the water shedding angle technique. A thorough investigation of the commercially relevant poly(ethylene terephthalate) fabric reveals an unparalleled long-term water resistance and stability of the superhydrophobic effect. Because of the special surface geometry generated by the nanoscopic, fibrous coating on the microscopic, fibrous textiles, the coated fabric remains completely dry even after two months of full immersion in water and stays superhydrophobic even after continuous rubbing with a skin simulating friction partner under significant load. Furthermore, important textile parameters such as tensile strength, color, and haptics are unaffected by the silicone nanofilament coating. For the first time, an in-depth characterization of the wetting properties, beyond simple contact angle measurements, as well as a thorough evaluation of the most important textile parameters is performed on a superhydrophobic fabric, which reveals a true potential for application.

1. Introduction

Surfaces with extreme water wetting properties have been of considerable interest within the scientific community for the last two decades and are gradually finding applications in many areas of everyday life. Non-wetting surfaces that exhibit self cleaning effects are inspired by natural surfaces such as the Lotus leaf.[1] On these so called superhydrophobic surfaces, drops of water remain almost spherical and easily roll off, removing dirt particles in their path. In view of the significant potential of such surfaces for numerous scientific and industrial applications, many strategies to create superhydrophobic surfaces have been published to date.[2–6] In most of these publications, the waterproofing of textiles is considered to be among the primary potential applications for the superhydrophobic effect. Textiles with a superhydrophobic coating could find applications as water resistant apparel and would generally be useful for any kind of application where textile surfaces are exposed to the environment. Additional benefits of the superhydrophobic effect on textiles could include a plastron layer. This thin layer of air forms on many natural superhydrophobic surfaces upon immersion in water. In some cases, as for the water bug (*Aphelocheiridae*), it is even indefinitely stable.[7] On one hand the ability to support a plastron layer would prevent a wetting of the textile even upon full immersion in water, on the other hand it would significantly reduce the frictional drag in water.

Despite the frequent reference to textile applications, only few reports exist that actually pertain to superhydrophobic textiles.[8–16] In many of these, only an initial characterization of the wetting properties of the resulting fabrics is performed, without reference to changes in important textile related properties such as tensile strength, color, haptics, etc. Also, the performance of the coating under chemical or mechanical stress or how long the superhydrophobic properties are maintained under prolonged exposure to water is not evaluated. A rough characterization of these parameters is necessary, however, to evaluate a superhydrophobic textile coating's potential for application.

A method that has been proven to produce superhydrophobic surfaces with exceptional properties is the so called silicone nanofilament coating.[17–20] With this technique, a dense layer of polyalkylsilsesquioxane filaments can be grown on a wide variety of materials in a gas or solvent phase coating setup at ambient temperatures.[17,18] The technique is simple, versatile, and inexpensive and the resulting superhydrophobic coatings show an excellent chemical and environmental stability.[21,22]

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Here we report the results of the application of the silicone nanofilament coating onto various textile substrates, including an in-depth characterization of the resulting superhydrophobic fabrics. Besides analyzing the wetting properties, which is not as trivial as generally assumed, various textile related parameters such as the tensile strength, the coefficient of friction, and the whiteness index were evaluated for the commercially relevant poly(ethylene terephthalate) (PET) fabric. In addition, the long-term water resistance of the superhydrophobic effect on textiles as well as the durability upon machine washing was evaluated.

In the process it was found that classical contact angle measurements were unsuited to reliably evaluate the wetting properties of superhydrophobic textiles and a new method was developed based on the water-shedding abilities of superhydrophobic textiles.

Aside from being the most extensive evaluation of a superhydrophobic textile coating to date, a potential of the silicone nanofilament coating for textile applications is demonstrated. Furthermore, the results clearly show that, with regard to the creation of a mechanically stable (abrasion resistant) superhydrophobic surface, a two tier roughness is essential.

2. Results and Discussion

2.1. A Simple One-Step Approach to Superhydrophobic Textiles

A total of 11 textile fabrics made from natural and man made fibers were coated with polymethylsilsesquioxane (PMSQ) nanofilaments under ambient conditions in the gas phase. Figure 1 exemplarily shows high-resolution scanning electron microscopy (SEM) images of four of the fabrics before and after coating as well as corresponding images of drops of water on the coated fabrics.

On all 11 fabrics, the characteristic nanofilament structure is observed and drops of water show very high contact angles. It is noteworthy that each individual fiber comprising the textile fabric is coated with a layer of nanofilaments. Even fibers deep inside the fabric are coated, which indicates that the mobility of the reactive precursors in the gas phase is sufficient to penetrate into the three-dimensional textile structure.

X-ray photoelectron spectroscopy (XPS) measurements confirmed the presence of silicon, carbon, and oxygen on the coated fabrics (Figure 2). The integrated peak intensities showed atomic ratios of 1/0.57/0.7 for O/Si/C on the coated fabric, which is in good agreement with the theoretical ratio of 1/0.66/0.66 for polymethylsilsesquioxane ($CH_3SiO_{3/2}$). The slightly higher oxygen and carbon content can be attributed to organic contamination as a result of storage of the sample at ambient conditions in the interval between preparation and measurement. The absence of a chlorine peak in the XPS spectra indicates that the trichloromethylsilane (TCMS) precursors are fully hydrolyzed during the coating reaction.

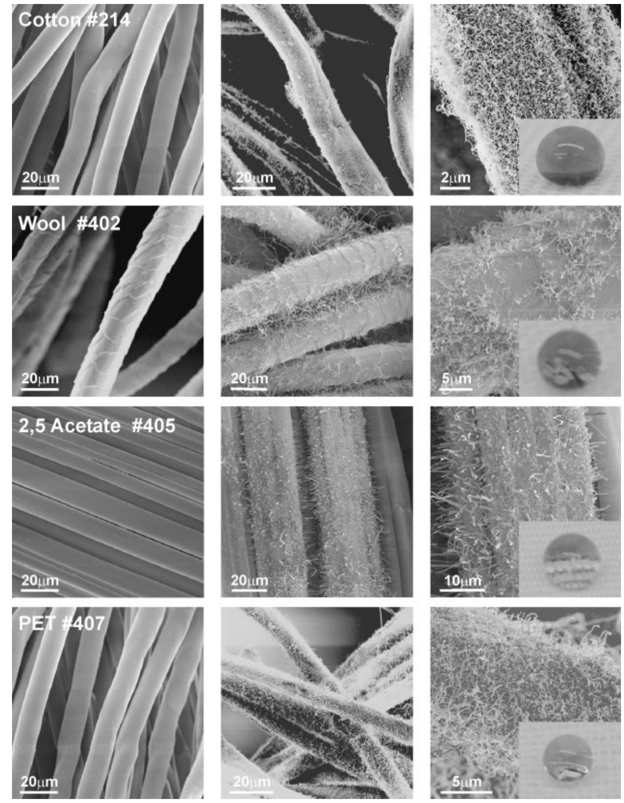

Figure 1. SEM images of textile fabrics: left: uncoated; middle and right: coated with silicone nanofilaments. Insets show a drop of water deposited on the respective coated fabrics.

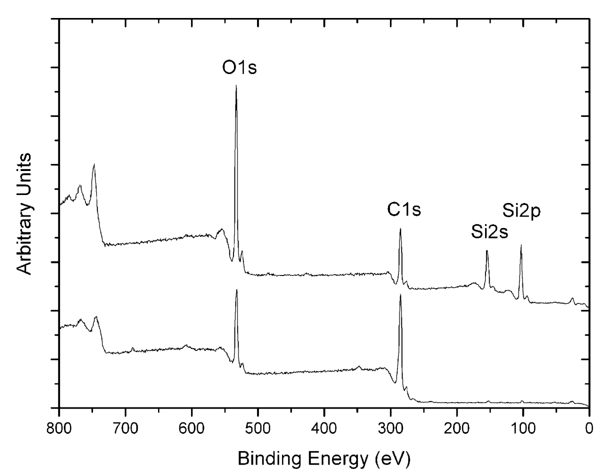

Figure 2. XPS spectra of an uncoated PET fabric (bottom line) and a fabric coated with PMSQ nanofilaments.

Although all textiles were successfully coated using identical coating parameters, the scanning electron micrographs (Figure 1) show that the quality of the coating, in terms of filament density, size, and distribution, varies significantly from one material to another. Also, the extent of the superhydrophobic effect differed considerably on the individual coated fabrics. Subjectively, no difference in the shapes of water drops placed on the various coated fabrics could be detected. However, on the surface of some fabrics even small drops would roll off upon slight inclination while others required a slight agitation to dislodge the smaller droplets.

When attempting to objectively determine the wetting properties of the coated fabric by classical contact and sliding angle measurements, it was found that these techniques were not suited for the macroscopically rough, pliant, and non-reflective textile surfaces. A reliable determination of the substrate baseline for the contact angle measurements was impossible, and single textile fibers sticking out of the fabric surface made sliding angle measurements unreliable. We therefore developed a new technique to evaluate the water repellent properties of superhydrophobic textiles. Details on the procedure can be found in a recent publication.[23] In brief, a drop of water is released onto the inclined substrate from a defined height and the minimum angle of inclination ('water shedding angle', WSA, ω) at which the drop completely rolls off the surface is determined. A similar procedure was employed by Wagner et al. to test the self cleaning capabilities of superhydrophobic surfaces.[24]

The WSA well reflects the qualitative differences in the water repellent properties of the superhydrophobic silicone nanofilament coated textiles (Table 1).

Clearly, the superhydrophobic effect and the resulting water repellent properties of the coated fabric are influenced by too many parameters to meaningfully interpret the individual results of the WSA measurements in the context of this work. The density, size, and distribution of nanofilaments, combined with the micro- and macroscopic structure of the textile fabric will affect the superhydrophobic effect. In addition, textile parameters such as fiber dimension, yarn, and weave will influence the WSA. For instance, open weave and knitted fabric structures will cushion drops of fluids and result in a higher WSA than a close weave or knitted fabric structure.

Nevertheless, the WSA angles clearly indicate that all coated textile materials show superhydrophobic properties and that, of these, the pure PET fabric shows the best water repellent properties. As PET is also one of the most commercially relevant textile materials, further studies on the wetting and textile related properties were performed on this substrate material.

Table 1. WSAs of various textile samples coated with PMSQ nanofilaments for water drops with a volume of 13 μL. For a full description of the samples please refer to the Experimental Section.

Sample no.	Polymer[a]	ω [°] (13 μL)
407	PET	2
403	silk	5
213	PET/CO (65/35)	10
408	PAN	10
402	wool	15
404	viscose	25
413	CO	25
214	CO	35
211	CO	35
414	wool	40
405	acetate	55

[a] CO: cotton, PET: polyester, PAN: polyacrylnitrile.

2.2. Wetting Properties of a Superhydrophobic PET Fabric

With a WSA of 2°, the polyester (PET) fabric #407 showed the best water repellent properties of all coated textiles (to give the reader an impression of the water adhesive properties in classical terms, the sliding angle on this sample was in the region of 15° for a 10 μL drop of water). Small drops of water appeared to float on the coated PET surface and a jet of water applied on the horizontal substrate would bounce off the surface without leaving a trace (Figure 3).

Upon immersion in water, a silver sheen covered the whole textile because of the total reflectance of light at the air layer trapped on the surface.[18,25] As already reported for glass samples coated with silicone nanofilaments,[18] this plastron layer was stable over many weeks (Figure 4). A coated sample removed from water after two months of full immersion was still completely dry to the touch.

So far only a few reports of stable plastron layers on artificial superhydrophobic surfaces exist.[25,26] Plastron layers are utilized in nature by some water-dwelling species such as the water spider to capture and trap air for breathing under water. They can also act as gas exchange barriers for oxygen and CO_2 exchange in water and enable insects like the water bug (Aphelocheiridae) to remain indefinitely submerged underwater (plastron respiration).[7,25,27] In respect to textiles, a stable plastron layer is very useful because it keeps the fabric dry under

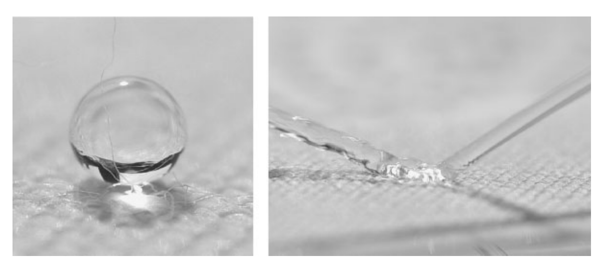

Figure 3. Water wetting properties of PET fabric #407 coated with PMSQ nanofilaments. Left: A 5 μL drop of water on the coated PET sample. Right: A jet of water bounces off the coated PET sample.

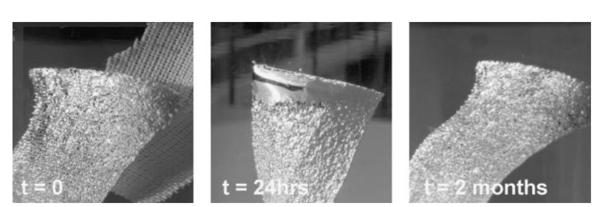

Figure 4. A superhydrophobic coated PET #407 fabric immersed in water. The left image also shows a piece of uncoated fabric immersed in water (background).

water, which could be interesting for swimwear applications. Also, a stable plastron layer improves the performance of breathable, waterproofing strategies such as Gore-Tex by preventing water from blocking the micropores and supporting a free gas exchange.[27] To the best of our knowledge, the performance of the coated PET fabric in terms of superhydrophobic properties and plastron stability is unparalleled so far.

In respect of the long term chemical and environmental durability of the silicone nanofilament coating, comprehensive studies performed on glass have shown that the coating is inert to organic solvents, has a long-term stability in mild aqueous pH and detergent solutions, a long-term stability towards environmental conditions during outdoor weathering, and shows a good resistance towards artificial weathering in a combined acid rain and UV testing chamber.[21,22]

One of the greatest problems facing the widespread application of superhydrophobic coatings is generally their low mechanical stability. In most cases even mild abrasive forces are sufficient to damage or destroy the delicate micro- and nanostructure that is required for the superhydrophobic effect.[3,4] On planar substrates, the silicone nanofilament coating faces the same problem. Even lightly rubbing a coated glass slide with a duster or with a finger leads to an immediate loss of superhydrophobic properties.[18] The coated textile fabrics, on the other hand, exhibited a very robust superhydrophobicity. Textile samples could be handled without any precautions and retain their superhydrophobic properties. Even continuous abrasion with a skin-simulating friction partner did not negate the superhydrophobic effect. Table 2 summarizes the wetting properties of a coated glass and a coated sample of PET #407 fabric before and after an abrasion test performed on a textile friction analyzer (TFA).[28]

The normal load used for these experiments corresponds to approximately 150% of the contact pressure that occurs when a person touches and rubs a fabric with the fingers[29] and is comparable to the pressure at the skin–mattress interface for a bedridden person.[28]

After 1 450 abrasion cycles the textile sample still shows a low WSA, whereas no WSA is measurable on the glass sample. Figure 5 shows SEM images of the abraded glass and textile sample as well as drops of water on the two substrates.

Clearly, the abrasive forces have completely destroyed the surface structure of the silicone nanofilament coating on the glass sample. A water contact angle of 95° indicates that a residual, hydrophobic layer remains on the abraded glass sample. In contrast, the nanofilament coating is mostly retained on the textile sample. Only those areas exposed to the abrasive forces show signs of damage while the majority of the filaments are protected by the 3D microstructure of the fabric. Since the residual layer after abrasion is also still hydrophobic, the overall superhydrophobic properties of the textile are retained.

Table 2. Wetting properties of a coated glass and a sample of PET #407 fabric: WSA (ω) for water drops with a volume of 5 and 13 μL, respectively, before and after the abrasion test (1450 cycles, normal load: 5 N) on a TFA.

Substrate	ω [°]			
	Before abrasion		After abrasion	
	13 μL	5 μL	13 μL	5 μL
Glass	1	2	–	–
PET # 407[a]	2	5	25	35

[a] The values are identical for samples rubbed along the weft and the warp direction.

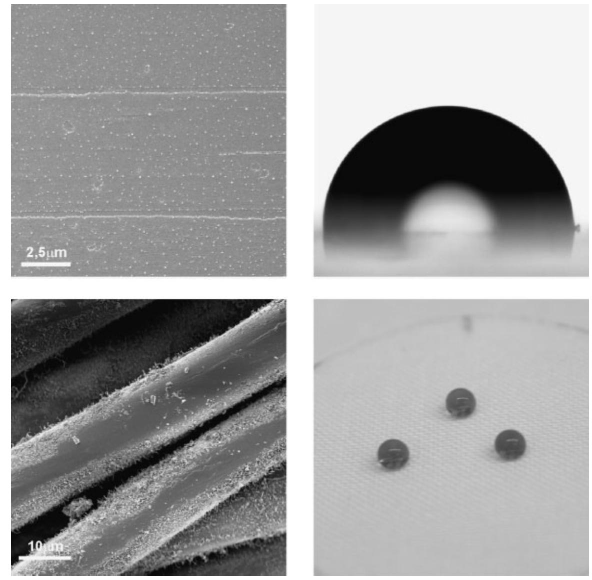

Figure 5. SEM images of coated samples after the abrasion test (Textile Friction Analyzer, 1 450 cycles, load: 5 N corresponding to a contact pressure of 7.8 kPa) and drops of water showing the wetting properties of the respective samples. Top: glass surface. Bottom: PET #407 fabric.

This effect of a combined 3D micro- and nanostructured system to achieve an abrasion resistant superhydrophobic surface is reminiscent of the strategy developed by nature. For instance, the lotus leaf surface protects its nanoscopic epicuticular wax crystals by an underlying, microscopically rough papillose arrangement of epidermal cells.[1,30] Upon mild abrasion, only wax crystals from the tops of the papillae are removed and the superhydrophobicity is maintained. Although it is generally assumed that this two tier roughness is the reason for the relative robustness of the superhydrophobicity of the lotus leaf,[1,30] the abrasion tests on the coated PET fabric are the first experiments performed on an artificial surface that support this assumption.

2.3. Textile Properties of a Superhydrophobic PET Fabric

The above performed experiments confirm that the superhydrophobic effect generated by the silicone nanofilament coating on a textile PET fabric shows exceptional and very useful qualities. However, any coating is useless if it alters the physico-chemical properties of the material in a way that makes it unsuitable for its original purpose. Following coating, the aesthetic properties of a fabric such as color and feel should remain unaffected. Likewise, mechanical properties such as tensile strength should not be altered by the coating. In addition, for any application in the apparel sector, the ability to launder the fabric in a household washing machine would be highly beneficial.

Colorimetric measurements (Table 3) reveal a very small total color difference (ΔE^*_{ab}) between the coated and the uncoated PET #407 fabric and only minor differences in the CIE whiteness index. It is worth noting that a total color difference of one ΔE^*_{ab} unit corresponds to a just noticeable difference by eye.[31] Furthermore, the main difference between the coated and the uncoated fabric pertains to the lightness vector L^* and not to the color-related coordinates a^* (red-green) and b^* (yellow-blue). Several samples of dyed PET fabrics were also coated successfully without a noticeable change in color.

Of primary importance to a textile coating is that it does not damage the textile fibers in a way that affects their mechanical properties. Ideally both the strength and flexibility of a fiber should be unaffected by the coating, but as much as a 10% difference in mechanical properties are still deemed acceptable and can be compensated using a denser weave of the fibers. Tensile strength measurements performed on a cotton and a PET fabric according to ISO 13934-1:1999[32] reveal that the silicone-nanofilament coating can have a completely different effect on the fabric strengths. Table 4 compares the elongation at break and tensile strength of the uncoated and the coated fabrics. In the case of the PET fabric, the mechanical properties are hardly affected by the coating process; both the tensile strength and elongation at break decrease by less than 10% after coating. The mechanical properties of the cotton fabric on the other hand are severely altered by the standard coating procedure (coating type I). Both elongation at break and tensile strength are reduced to a value that makes the fabric useless for any real application. This loss of performance is a result of the generation of hydrochloric acid during the standard coating process, which degrades the acid sensitive cotton fibers. If the amount of hydrochloric acid generated in the coating process is reduced by replacing most of the trichloromethylsilane (TCMS) with methyltrimethoxysilane (MTMS), the coated cotton fabric gains in stability (coating type II). But to make the coating truly applicable to acid sensitive materials, an alternative coating process that, for example, relies on a base-catalyzed instead of an acid-catalyzed initial hydrolysis would need to be developed.

When touching the coated and the uncoated samples, no difference in the feel of the fabrics was noted. However, analysis of the friction data recorded during the abrasion testing of the fabric showed that both the static and the dynamic coefficient of friction (COF) increase significantly for the coated fabric (see supplementary information). Nevertheless, stringent conclusions regarding the influence of the higher COF of the coated versus the uncoated PET fabric on the tactile properties (haptics) could not be drawn. The tactile properties of a textile fabric are a result of various structural, mechanical, and surface parameters,[29] the friction properties being only one of them, and a detailed haptic analysis would require comprehensive subjective sensory assessments by human test subjects.

Table 3. Colorimetric measurements on coated and uncoated PET #407 fabric. L^*, a^*, b^*: basic coordinates in the CIELab Color space; ΔE^*_{ab}: total color difference of the two materials; CIE WI: CIE whiteness index.

Fabric	L^*	a^*	b^*	ΔE^*_{ab}	CIE WI
PET #407 (uncoated)	93.01	−0.75	3.12		68.5
PET #407 (coated)	93.99	−0.77	2.82	1.03	72.3

Table 4. Tensile strength measurements on silicone-nanofilament-coated cotton (#413) and PET (#407) fabrics.

Fabric	Coating type	Tensile strength [N cm^{-1}]	Elongation at break [%]
PET #407	uncoated	128 ± 3	39.0 ± 1.0
	I	120 ± 7	37.6 ± 1.0
Cotton #413	uncoated	83 ± 5	33.3 ± 1.3
	I	1.4 ± 0.4	5.9 ± 0.9
	II	11.3 ± 0.6	21.0 ± 0.5

During machine washing, three factors facilitate the cleaning of a fabric: heat, mechanical forces, and chemicals. Unfortunately all of these factors can also damage a textile or a textile coating. While the PMSQ nanofilament coating is insensitive to heat below 200 °C,[18] both mechanical friction and the cleaning detergents included in the washing formulation[21] could lead to a loss of superhydrophobic properties. To evaluate the effect of a combined mechanical and chemical stress during a washing cycle on the superhydrophobicity of the coated PET fabric, it was subjected to a mild standardized machine washing procedure in accordance with ISO 6330:2000.[33] After the washing cycle, the coating shows clear indications of both a mechanical and a chemical degradation (Figure 6).

Opposed to the samples of the abrasion test, the silicone nanofilament coating is damaged on all areas of the textile fibers including deeper regions of the 3D microstructure of the fabric. The slightly etched and melted look of the nanofilaments on the washed PET fibers is reminiscent of the degradation observed during immersion of coated glass samples in basic media.[21] Considering that the washing liquor has a pH of 9–11 because of the washing agent added in the washing cycle, this is not surprising.

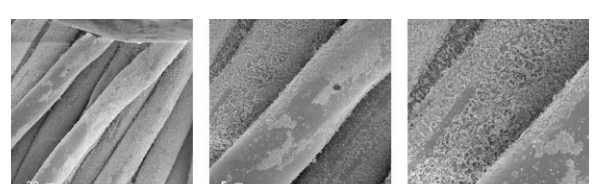

Figure 6. SEM images of a coated PET #407 fabric after washing at 30 °C according to ISO 6330:2000 [33].

Water-shedding measurements performed on the washed samples resulted in a WSA of 20° for a 13 μL drop, and 25° for a 5 μL drop of water. Even though, judging from the electron microscopy images, the degradation of the coating after washing appears to be more severe than in the case of the abrasion testing, the water-shedding abilities of the washed samples are superior to those of the abraded samples. However, if a drop of water was suspended on the washed samples it would only maintain a high contact angle for several tens of seconds before being completely wicked into the fabric (a movie of this behavior is supplied in the Supporting Information). On the abraded sample (or any of the freshly coated samples), on the other hand, drops of water maintained a high contact angle indefinitely. It is clear from these observations that the WSA only reflects the short term resistance to wetting and must be supplemented by additional wetting experiments like sessile drops or water immersion to judge the overall wetting behavior of a substrate. Also, the sessile drop experiment indicates that for an application where washing in a washing machine with basic cleaning detergents is required, the silicone nanofilament coating needs to be improved in terms of stability. Nevertheless, it is remarkable to what extent the coating retained its water repellent properties even under such demanding conditions. The use of acidic instead of basic detergents in the washing cycle might further improve the coatings' durability as it is significantly more stable in acidic than in basic media.[21]

3. Conclusions

We have performed extensive studies on a superhydrophobic silicone nanofilament coating applied to textiles. The coating offers many benefits over other coating techniques in the context of textile coatings. The coating process is simple and inexpensive and can be applied in a gas or solvent phase under ambient conditions. In the coating process, each individual textile fiber is coated with a layer of hydrophobic nanofilaments. The technique is, therefore, not reliant on any special fabric structure to generate the superhydrophobic effect. The filaments are chemically attached to the surface unlike, for instance, in many sol-gel coating processes, where nanoparticles are only physically adsorbed. For a significant number of fabrics that consist of commercially relevant polymers coated in the course of this work, no pre or post processing of the substrates was required. The procedure is, therefore, a true one-step approach to superhydrophobic textiles.

Because traditional contact angle measurements were found to be unsuitable for a meaningful evaluation of the wetting properties of superhydrophobic textiles, a new technique was employed that evaluates the water shedding abilities of a fabric.

Detailed analysis of the wetting properties of a coated polyester fabric revealed some of the strongest water repellent properties ever reported for a textile coating, especially in terms of long-term water resistance. A stable plastron layer was supported for at least two months of full immersion in water and the fabric emerged completely dry after this period.

Despite an inherent fragility of the silicone nanofilaments, the superhydrophobic effect was very robust on the coated textiles. Even continuous abrasion with a skin-simulating friction partner under a significant load did not result in a loss of superhydrophobic properties. Electron microscopy revealed that the silicone nanofilaments situated in the underlying microstructure of the textile fabric are effectively protected from abrasive forces, similar to the two tier roughness strategy of the lotus leaf.

In addition to the exceptional wetting properties of the silicone nanofilament coating, extensive studies on the textile properties of the coated fabrics revealed that the coating does not significantly influence the mechanical and optical properties of the textile. Although the coefficient of friction increased noticeably because of the coating, preliminary sensory tests did not reveal a noticeable influence on the haptic of the fabric.

Overall the silicone nanofilament coating has proven to be an interesting candidate as a textile finish for super water repellent fabrics. Extensive studies on both the wetting properties and textile related properties (often missing in related publications) indicate that the coating is superior to any other superhydrophobic textile coating published to date. Besides an obvious application for non-wetting fabrics, the unmodified coating on textiles could also be employed for oil–water separation strategies such as have been demonstrated on other hydrophobic/oleophilic coatings.[34,35]

4. Experimental

Substrates and Chemicals: A total of 11 different textile materials (Table 5), comprising natural and man made polymers with varying weave, thickness, and density, were provided by the EMPA Testmaterials AG (Mövenstrasse 12, 9015 St. Gallen, Switzerland). TCMS (97%) and MTMS (97%) were purchased from ABCR (Germany), handled under water free conditions and used without further purification.

Sample Preparation: Preparation of the initial superhydrophobic silicone nanofilament coating is described elsewhere in detail [18]. In brief, textile samples of varying sizes were introduced in a reaction chamber and equilibrated at a relative humidity of 40–50% and ambient temperature. To initiate the coating reaction 300 μL of reactive silane was introduced into the reaction chamber. In the standard coating type I, the coating formulation comprised of pure TCMS. For coating type II, 280 μL of TCMS was replaced with MTMS in the coating formulation.

Measuring the WSA: Textile samples were glued onto glass cover slips with double sided adhesive tape and placed on a custom built tilting table. A syringe was mounted above the tilting table with a fixed needle to a substrate distance of 1 cm. The syringe was positioned in a way that a drop falling from the needle would contact the substrate 2 cm from the bottom end of the sample. Two needles with inner diameters of 130 μm (Hamilton #90531) and 250 μm (Krüss #NE 43) were used to produce water drops with volumes of 5 ± 0.3 and 13 ± 0.3 μL, respectively. To control the volume of the drops released from the needle, a drop of 4.5 or 12.5 μL volume was produced at the

Table 5. Textile substrates used for coating with silicone nanofilaments.

EMPA Testmaterials Product No.	Product name	Type of weave	Area weight [g m^{-2}]	Specifications according to
#211	Cotton fabric, percale	plain weave	90	
#213	Polyester/cotton fabric (65/35)	plain weave	165	
#214	Cotton twill fabric	twill	210	
#402	Wool muslin	plain weave	120	ISO 105-F01
#403	Silk Crêpe	crêpe	70	ISO 105-F06
#404	Viscose spun, shiny	plain weave	120	ISO 105-F02
#405	2,5 Acetate, endless fibers	taffeta weave	125	ISO 105-F07
#407	Polyester Dacron, type 54 spun	plain weave	140	ISO 105-F04
#408	Polyacrylnitrile Orlon, type 75 spun	plain weave	150	ISO 105-F05
#413	Cotton for crockmeter	plain weave	100	ISO 105-F09
#414	Wool tricot JWS SM29 (Hercosett superwash)	knitted fabric	350	

needle tip using the automated syringe control of an OCA 20 contact angle system (Dataphysics). The drop was then successively expanded in steps of 0.1 μL until it detached from the needle.

To determine the WSA, measurements were started at an inclination angle of 85°. Drops of water were released onto the sample at a minimum of five different positions, each 2 cm from the bottom end of the sample. If all drops completely bounced or rolled off the sample, the inclination angle was reduced by 5° and the procedure repeated until one or more of the drops would not completely roll off the surface. This could either be evident from the whole of the drop coming to rest on the surface after rolling a short distance or from parts of the drop sticking to the surface at the impact point or on the path down the incline. The lowest inclination angle at which all the drops completely rolled or bounced off the surface was noted as the WSA.

Plastron Stability: To evaluate the stability of the gas layer that forms upon immersion of silicone-nanofilament-coated substrates in water, a 2×5 cm^2 sample of coated PET #407 fabric was immersed in a beaker of deionized water and pictures taken over the course of two months. Weights were attached to the fabric sample to keep it submerged.

X-Ray Photoelectron Spectroscopy (XPS): XPS measurements were performed using a PHI LS 5600 instrument with a standard Mg Kα X-ray source. The energy resolution of the spectrometer was set at 0.4 eV per step at a pass energy of 93.9 eV for survey scans and 0.125 eV per step and 29.35 eV pass energy for region scans. The X-ray beam was operated at a current of 25 mA and an acceleration voltage of 13 kV. Charge effects were corrected using carbon $1s = 285.0$ eV. The concentrations of the surface species were determined using CasaXP software (peak areas were evaluated using the instrument specific relative sensitivity factors).

Colorimetric Measurements: The CIE whiteness index and the CIELAB color difference were evaluated on four-ply samples using a Datacolor Spectraflash 500 spectrophotometer with Datacolor Tools evaluation software (Datacolor, Dietlikon, Switzerland). Measuring geometry d/8°, CIE illuminant D65, visual field 10°, without UV filter.

Tensile Strength According to ISO 13934-1:1999: The tensile strength and the elongation at break of coated and uncoated samples were evaluated on a INSTRON 4502 universal testing instrument (Instron Corporation, Norwood, MA, USA) in the style of ISO 13934-1:1999 [32] using the following parameters: testing direction: weft; sample width: 23–56 mm; initial length of the sample: 50 mm; pretension: slack mounting of the samples; rate of extension: 50 mm min^{-1}. Testing atmosphere: temperature: 23 ± 1 °C; relative humidity: 50 ± 2%. Tests were carried out in triplicate. All samples were preconditioned in the testing atmosphere for at least 24 h before testing.

Friction Test: Frictional load was applied to the samples using a TFA primarily designed for the instrumental simulation of skin-fabric contact and friction. A skin-simulating polyurethane-coated polyamide fleece (Lorica Soft, Lorica Sud, Milano, Italy) was used as the friction partner for the silicone nanofilament coated substrates.

The TFA works on the reciprocating sliding principle: the lower friction partner (skin model) is mounted on a reciprocating sled (metallic block) that oscillates with a given frequency, which corresponds to a linear sliding velocity. The upper friction partner (textile sample) is connected to an elevation arm that provides enhanced friction test performance by applying a vertical load over an adjustable force range. A detailed description of the TFA can be found elsewhere [28]. All samples were mounted on the sample holders using double-sided adhesive tape.

The friction experiments were performed using the following experimental parameters: normal load: 5 N; oscillating frequency: 1.25 Hz; stroke: 20 mm; resulting sliding velocity: 62 mm s^{-1}; number of cycles: 1450; textile standard climate (20 ± 1°°C, 65 ± 2% relative humidity). All samples were preconditioned in the testing atmosphere for at least 24 h before testing.

Machine Washing According to ISO 6330:2000: Washing was performed according to ISO 6330:2000 [33], procedure 8A (delicate cycle, 30 °C, total amount of polyester ballast: 2 kg, total amount of washing agent: 28 g) in a reference washing machine (Wascator FOM 71 Lab; Electrolux Laundry Systems, Hvidovre, Denmark). For the washing process, a 6×14 cm^2 sample was stitched onto a piece of ballast.

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