

École polytechnique de Louvain

Effect of fabric texture and coating nature on water repellency

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Abstract

Water-repellent properties allow clothing and outdoor equipments to protect us from being wet and the textile industry still focuses on the design of clothes showing such properties. Well-established types of coatings using long chain perfluorinated compounds (C6 and C8) were used so far by the textile industry. However, because of the environmental issues these coatings cause and the risks they present for human health, several regulatory actions were taken to forbid the usage of PFAOS. Therefore, alternative solutions must be found to replace the coatings using these chemicals.

This study compares the performances of three types of alternative chemicals that can be used to provide water-repellent properties to fabrics. In addition, we studied the effect of surface texture on the resulting hydrophobic properties of the coated fabrics. To do so, the three different coatings were prepared from commercial formulations. The prepared coatings were deposited on seven different fabrics with different surface roughness. We used the roughness factor r defined by Wenzel among all the parameters available to describe the surface roughness.

To determine the roughness factor of the uncoated and coated fabrics, we used stylus profilometry and Atomic Force Microscopy (AFM). Stylus profilometry measurements showed that the fabrics have a macroscale roughness ranging from $r = 1.16$ to $r = 1.86$. On the other hand, the scans performed by AFM showed that the fibers do not contribute to the surface roughness of the fabrics since the fibers appeared to have roughness factor equal to one.

The assessment of the water-repellent properties of the coated fabrics was performed by measuring the contact angle, the static roll-off angle and the dynamic roll-off angle for each sample. These measurements revealed that rougher samples are more hydrophobic, i.e., an increasing roughness results in increasing water-repellent properties. Moreover, the high contact angle measured for rougher samples ($\sim 140^\circ$) showed that only the choice of an appropriate weave pattern with a defined roughness is enough to provide desired hydrophobic properties to fabrics (after being coated). Finally, these measurements revealed that the coating nature reduces or increases the static and dynamic roll-off of the fabrics. Indeed, one coating showed lower static and dynamic roll-off angles for all the studied fabrics compared to two other coatings.

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Symbols

Symbol	Description	Unit
γ_{lv}	Surface energy of the liquid-vapor interface	J m^{-2}
γ_{sl}	Surface energy of the solid-liquid interface	J m^{-2}
γ_{sv}	Surface energy of the solid-vapor interface	J m^{-2}
θ	Measured contact angle	deg
θ_{CB}	Cassie-Baxter contact angle	deg
θ_Y	Young-Dupré contact angle	deg
θ_W	Wenzel contact angle	deg
f	Fractional surface area	/
f_{lv}	Fractional surface area of the liquid-vapor interface	/
f_{sl}	Fractional surface area of the solid-liquid interface	/
h	Height	m
h_0	Zero height level defined by the stylus profilometer	m
L	Sampling length	m
r	Wenzel roughness factor	/
R_a	Arithmetic average height	m
R_q	Root mean square roughness	m
S	Actual surface area	m^2
S_0	Projected surface area	m^2
S_a	Arithmetic average height over a surface area	m
S_q	Root means square roughness over a surface area	m

Introduction

Everyone has once experienced the feeling of being cold due to wet clothes. Seamen are particularly concerned by this problem and the first mentions of water protective clothing appeared in the 15th century, when sailors impregnated their clothes with linseed oil, animal fat or wax. Nowadays, the textile industry still focuses on the design of clothes presenting water-repellent (i.e. hydrophobic) properties. However, on the 13th of June 2017, the European Commission decided to ban (starting from 2020) the chemicals currently often-used coatings, i.e. long chain perfluorinated compounds (C6 and C8), that provide water-repellent properties to fabrics and other types of equipments. These compounds appeared to be bioaccumulative, persistent and dangerous for aquatic organisms and human health. These chemicals were very efficient to provide water-repellent and oil-repellent properties to textiles. Nevertheless, combining oil and water repellency is very complex and water repellency remains the priority. Therefore, this study focuses on three alternative fluor-free formulations that can be used to prepare coatings which provide water-repellent properties to fabrics. The importance of fabric texture and the influence of this parameter on the final hydrophobic characteristics of fabrics is especially evaluated.

To do so, on the one hand, seven different fabrics each having a different surface texture, were studied in parallel. On the other hand, three commercial formulations containing chemicals of different natures were used to prepare three different coatings. The first step of this study was to characterize the surface texture of the fabrics before and after coating deposition. The surface roughness is one of the parameters that permit to describe surface texture and was thus evaluated for the different fabrics. Two techniques were used to determine the roughness of the different fabrics, stylus profilometry and Atomic Force Microscopy (AFM). The data extracted via the first technique allowed us to determine the macroscale roughness of the fabrics. AFM measures micro and nanoscale features at the surface of the fibers which make the fabric and allowed us to compute the microscale roughness of the fabrics. These two types of measurements were performed before and after coating of the fabrics. The assessment of the water-repellent properties of the coated samples was done through the measurements of the contact angle, the static roll-off angle and the dynamic roll-off angle. These three different types of measurements allowed us to compare the samples and to study the effect of the surface texture on the resulting water-repellent properties of the fabrics.

Furthermore, they offered the possibility to compare the different coatings and to determine whether one of them provides better hydrophobic characteristics to fabrics.

This Master's thesis is divided in three main chapters. First, the state of the art covers the important concepts useful for the reader to understand the subsequent chapters. Surface roughness, surface-water interaction, coatings providing hydrophobic properties and information about weave patterns are described in this chapter. The second chapter presents the materials, processes and techniques used to prepare and characterize the samples. More specifically, the different fabrics tested are presented as well as the coating processes and the measurements procedures. The last chapter presents and discusses the different results obtained from stylus profilometry, AFM and contact angle measurements. Finally, this Master's thesis ends with conclusions and suggestions for further work.

Chapter 1

State of the art

The state of the art is divided into three sections and the first one concerns the fabric texture. The fabric texture is characterized by different parameters, among which the roughness will concern us more specifically. The roughness greatly affects hydrophobic properties and it is therefore discussed here in detail. Its definition and several methods to characterize and determine the roughness of surfaces are presented.

The second part first deals with the interaction of water with a hydrophobic surface. Existing models describing this interaction for hydrophobic surfaces allow us to understand more deeply the behaviour of liquids when they are in contact with a solid surface and the importance of the surface roughness. The surface-water interaction is closely related to the solid surface characteristics that can be changed with coatings for instance. The other aim of the study is to assess the influence of the coating nature on the hydrophobic properties they confer to fabrics. Hence, a discussion regarding the coating requirements and characteristics follows in the last part of this chapter. The drawbacks and the further developments of low surface energy coatings ends this chapter.

The third and last part of this chapter is dedicated to the description of the two different types of weave patterns encountered in the studied fabrics.

1.1 Roughness definition and characterization

The interaction of a solid with its environment occurs by means of its surface. Therefore, the surface properties of the solid have to be known to understand its behaviour with the surrounding medium. Several physico-chemical parameters take part in the properties of surfaces. However, in the frame of this study, we first focus on a fundamental property of solid surfaces in general which is the surface roughness (texture). The importance of this parameter is highlighted through this study. The purpose of this section is to define this parameter and to describe how it can be calculated. Finally, different instruments that can be used in order to estimate the roughness of a solid surface are presented.

1.1.1 Definition and computation

Surface roughness can be defined as the vertical deviations of a real solid surface from its plane form. From there, Wenzel defined the surface roughness of a solid by a roughness factor r , which is defined as the ratio between the actual (S) and the projected solid surface area (S_0) [1]:

$$r = \frac{S}{S_0} = \frac{\text{actual surface area}}{\text{projected surface area}} \quad (1.1)$$

Should this ratio be equal to one, the surface is considered as completely smooth. On the other hand, the higher the value of r , the rougher the surface. This mathematical definition allows us to understand what surface roughness represents. However, one cannot calculate it directly from this relationship. Indeed, the real surface geometry of a solid is usually complex, random and difficult to define. A finite number of parameters are therefore not sufficient to describe real surfaces. This led to the development of different roughness parameters which partially describe the surface roughness. [2–4]. The large number of existing roughness parameters shows the complexity to describe precisely the surface roughness but also the importance that is given to this feature because of its influence on the resulting interaction(s) of a solid with its environment.

The roughness parameters are divided in three different categories, amplitude parameters: spacing parameters and hybrid parameters. Yet, amplitude parameters are considered as the most appropriate to characterize the surface topography. They are indeed used to quantify the height variations of the surface, relative to a reference plane, that are measured along a line profile or a map of the surface (parallel line profiles). The two most commonly used statistical height descriptors are the arithmetic average height (R_a), also known as the center-line average (CLA), and the root mean square roughness (R_q) [2–4]. The first one, R_a , is defined as the average absolute deviation from the mean line over a defined sampling length (L) and is illustrated in Figure 1.1. The second one, R_q , is the root mean square (standard) deviation of the distribution of surface heights from a mean line over the sampling length [2–6]. The main difference between these two parameters is the sensitivity to large deviations from the mean line. R_q is more affected by important height variations compared to R_a . The mathematical definition and the digital implementation are slightly different for both parameters as can be seen respectively from equations 1.2, 1.4 and 1.3, 1.5. In equations 1.3 and 1.5, n represents the number of sampling points per line profile.

$$R_a = \frac{1}{L} \int_0^L |z(x)| dx \quad (1.2)$$

$$R_a = \frac{1}{n} \sum_{i=0}^n |z(i)| \quad (1.3)$$

$$R_q = \sqrt{\frac{1}{L} \int_0^L (z(x))^2 dx} \quad (1.4)$$

$$R_q = \sqrt{\frac{1}{n} \sum_{i=0}^n z^2(x_i)} \quad (1.5)$$

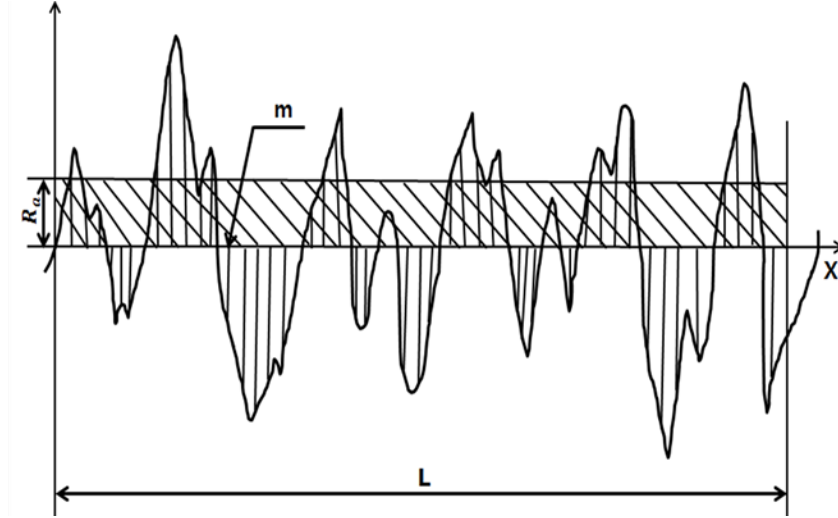


Figure 1.1 – Example of a line profile in which the arithmetic average height, R_a , is indicated as well as the sampling length, L . The reference plane (or mean line) is indicated as 'm' in the image [7].

R_a and R_q are parameters that can be computed from a line profile or from the surface topography of the whole surface [2–4]. As previously mentioned, a map scan of a solid surface is constituted of parallel line profiles. Therefore, the calculations of R_a and R_q are carried out on all of these line profiles. The extension of the arithmetic average height is referred to as S_a while for the root mean square roughness it is S_q . On the one hand, S_a represents the average of the absolute values of $z(x, y)$ in the measured area. On the other hand, S_q represents the standard deviation of heights for a given area. The variable m introduced in equations 1.7 and 1.9 refers to the number of parallel line profiles [5, 8]. Adjustments to the two-dimensional equations are as follows:

$$S_a = \frac{1}{A} \iint_A |z(x, y)| \, dx dy \quad (1.6)$$

$$S_a = \frac{1}{nm} \sum_{i=0}^n \sum_{j=0}^m |z(x_i, y_j)| \quad (1.7)$$

$$S_a = \sqrt{\frac{1}{A} \iint_A z^2(x, y) \, dx dy} \quad (1.8)$$

$$S_a = \sqrt{\frac{1}{nm} \sum_{i=0}^n \sum_{j=0}^m z^2(x_i, y_j)} \quad (1.9)$$

Only two different types of amplitude roughness parameters have been detailed here but one has to keep in mind that several other roughness parameters exist. The skewness (S_k or R_{sk}), the Kurtosis (K or R_{ku}), the ten-point height (R_z), maximum peak to valley height (R_{max} or R_{ti}), *etc.* are other examples of amplitude parameters.

The second category of parameters used to describe the surface roughness are encompassed under the name of spacing parameters. They evaluate the horizontal characteristics of the vertical surface deviations along the line profile [2] as the number of peaks per line profile for instance, called the peak count (P_C). Other well-known spacing parameters are, for example, the high spot count (HSC), the peak density (N_p or m) and the zero crossing density (N_0 or $n(0)$) [2–4].

Finally, the last type of roughness parameters is the category of hybrid parameters. Examples are the mean slope of the profile (Δ_a), the root mean square slope of the profile (Δ_q) and the profile slope at mean line (γ) [2–4]. Numbers of other roughness parameters. They were all introduced gradually in order to try to describe as precisely as possible the surface roughness.

Despite the number of existing roughness parameters, in the frame of this study, our aim is to provide a quite accurate value for the Wenzel roughness factor defined in equation 1.1. For this purpose, we need to measure and calculate the actual surface area. This is possible by using 3D surface scans measured with Atomic Force Microscopy (AFM) and stylus profilometry (see section 1.1.2). From these measurements, we can extract the position of each data point (x, y) and the height (h) for each position. In other words, we can measure the height variation as function of x and y positions, $h(x, y)$. Considering the definition of the roughness factor r in equation 1.1, we need to determine the actual area of the surface. This can be done through the surface integral of the scalar function $h(x, y)$. This particular surface integral, written in equation 1.10, is computed over the projected solid surface area S_0 and allows us to obtain S which provides the actual surface area requested to compute the r factor [9]. Having both S and S_0 , one can estimate r and the surface roughness. Yet, the data obtained from AFM and stylus profilometry are discrete signals and thus provide a discrete image. Applying the mathematical definition in practice, amounts to evaluate the integrand for every pixel of the image. By doing so, a roughness factor is calculated for every pixel of the image. The final roughness factor r is then the arithmetic average of the roughness factors computed for each pixel.

$$S = \iint_{S_0} \sqrt{1 + \left(\frac{\partial h}{\partial x}\right)^2 + \left(\frac{\partial h}{\partial y}\right)^2} dx dy \quad (1.10)$$

1.1.2 Techniques for roughness measurement

The previous section has allowed us to understand the concept of surface roughness through one of its possible definitions and the several roughness parameters that exist to characterize a surface. The methods and instruments that can be used to acquire the data required to determine roughness parameters still need to be discussed. This section will provide an overview of several techniques that can be employed for roughness measurements. One needs to keep in mind that the different instruments provide roughness measurements for areas of various scales and sometimes require specific surface properties (e.g., a conductive surface). Consequently, the method that will be used also depends whether one wants to measure nano, micro or macroscale roughness features. Naturally, the advantages and limitations of each method are also influencing the choice of the method.

Mechanical stylus profilometry

The most widely used method is probably the mechanical stylus profilometry. For this technique, a stylus with a tip of specific radius at its end is moved at constant speed over the surface. The tip applies a constant force on the sample and the vertical motion of the stylus to maintain this force constant is recorded. In most cases, the stylus is coupled with a linear variable differential transformer (LVDT) sensor. It can also be an optical or capacitance sensor. These various types of sensors monitor the vertical motion of the stylus [4, 6, 10, 11]. The resulting outcome is a time-varying electrical signal that represents the surface profile. This same signal needs then to be amplified and digitized such that it can be used for statistical analysis.

The performance and accuracy of the stylus profiler resides in the diameter of the tip and the precision of the applied force to the stylus. The smaller the diameter of the tip, the smaller the grooves that can be detected. A conical shape with a ballpoint tip is considered ideal for a stylus [4]. The precision to maintain the applied force on the sample surface is relative to the sensors sensitivity. Therefore, the higher the precision, the higher the sensitivity to the vertical deviations of the surface and thus, the higher the vertical resolution.

Stylus profilers are used for simple line scans but also for three-dimensional surface scans. This can be done by executing two-dimensional scans in the y axis direction and shifting the starting position between each line profile by a few micrometers in the x axis direction. All the parallel line profiles are then placed next to each other to reconstruct the surface scan.

The main advantage of the stylus profiler is to provide a reliable measurement since it is in direct contact with the surface. Moreover, it is capable of scanning the sample over a long distance and the scanning is independent of the surface properties. However, being in direct contact with the sample can cause damage to the solid surface. In addition, the measurement takes time and its resolution is limited by the tip radius. The wear of the stylus also needs to be taken into account. Yet, the vertical resolution can be of the order of a few nanometers while the lateral resolution depends on the radius of the tip. [4, 6, 10–12].

This instrument was used during our study and its experimental usage is further developed in section 2.3.

Optical methods

In contrast with a contact method like the stylus profilometry, optical methods have the important advantage of not being in direct contact with the sample. Hence, these methods are non-destructive and faster. Optical methods can be divided in two different categories: geometrical and physical methods. Taper-sectioning and light-sectioning are two examples of geometrical methods. Since these are not the most common ones, we will not develop them here. Physical methods on the other hand, include mostly light interference methods but also speckle pattern methods and focus sensing methods for instance [4–6, 10, 12–14].

Optical interferometry is the crucial physical principle used in many physical methods. This principle is based on the formation of an interferogram. Further treatment of the interferogram allows to image the surface profile and estimate the roughness [4, 5, 10, 13]. To obtain an interferogram, we can combine a light source, a beam splitter, a reference surface (flat), the solid sample and a photodetector or camera. Assembled together, these parts form a two-beam interferometer (Figure 1.2). Most modern devices that use optical interferometry are based on this original instrument. The two-beam interferometer illustrates the basic principle of optical interferometry and devices that result from it. A simple schematic representation with the main parts is depicted in Figure 1.2.

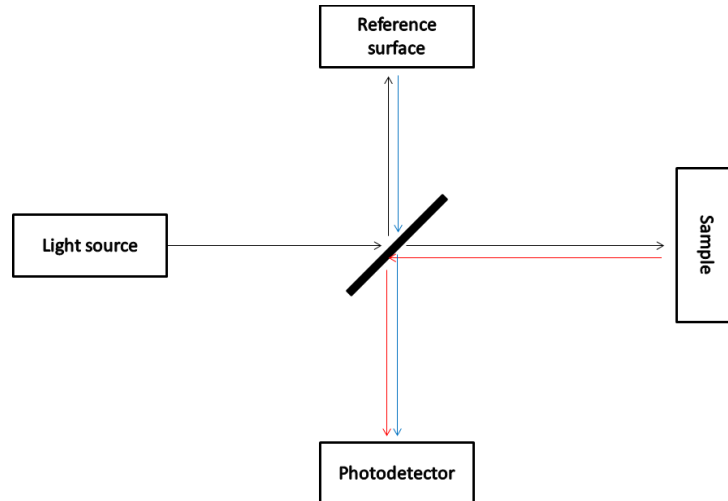


Figure 1.2 – *Schematic description of a two-beam interferometer.*

In the case of a two-beam interferometer, a source emits light with a defined wavelength. Once this incoming beam reaches the beam splitter, half of it is directed towards a reference sample (usually flat) while the other half is oriented towards the surface of the analyzed sample. Both surfaces reflect the incoming light beam and these reflected beams are reunited at the beam splitter before being directed towards the photodetector. The interference between these two different incoming signals results in an interferogram. The interference pattern usually leads to parallel fringes. Profile extraction

is possible if the reflecting properties of the sample are homogeneous. If so, any difference in the path length traveled between the two surfaces and the beam splitter results in a phase shift between the two reflected beams. Destructive or constructive interference occurs and, therefore, the interferogram mirrors varying surface heights [4, 6].

Nowadays, more advanced interferometry techniques have grown based on the principle of the two-beam splitter.

White light interferometric microscopy (WLI) is one of them. This technique uses a broadband white light source to illuminate the two surfaces and allows high vertical resolution (for very rough surfaces). Here, the degree of fringe coherence is analyzed and the principal fringe actually describes zero path difference between both surfaces. [4-6, 10, 12, 13].

Phase shifting Interferometry (PSI) is another example. The time-variable-phase between the two interfering beams is changed by 90° for each pixel. Mathematical treatment of the resulting signal recorded on the photodetector allows to determine the phase at each point of the interference pattern. The corresponding height distribution can then be determined. Interferometry techniques have been widely developed and modern optical profilers can combine some of these techniques [4, 6, 10].

Speckle pattern methods use a light source that emits partially coherent light. The scattering of coherent light and the interference between the reflected beams will form a random pattern of bright and dark regions called speckle. The scattering is influenced by the surface roughness and therefore, the speckle can be related to the surface roughness. Relating the speckle and surface roughness is called the speckle correlation measurement [4, 13, 14].

Focus sensing methods are also an alternative to interferometry techniques. For instance, confocal microscopy uses apertures to determine the height of a surface point. A light beam is focused onto a small spot of the surface and the reflected beam passes through an aperture which is set at the exact focus position. The surface is then scanned with this light beam and height variations induce a change of the focus position. Since the aperture does not change position during the scanning, the light intensity passing through the pinhole varies with the surface roughness. The variation of the light intensity signal is thus the direct reflection of the surface roughness. The main limitation with this technique is the spot size of the focused beam that determines its resolution [5, 10, 13].

Scanning Probe Microscopy methods

Scanning Probe Microscopy (SPM) methods offer the possibility to measure details at the nanometer and even sub-nanometer scale. These devices allow to reveal nanoscale topographical features which can be important for the estimation of the surface roughness at the very small scale. The two main devices used for SPM are the Scanning Tunneling Microscope (STM) and the Atomic Force Microscope (AFM) [4, 5].

Scanning Tunneling Microscopy is based on a quantum phenomenon, namely the tunneling current. When a potential difference is applied between two electrodes that are separated by a thin insulating film, a current flows between both electrodes if the potential difference is high enough. This current is called tunneling current since electrons cross the potential barrier (insulating film) to flow from one electrode to the other [4, 6, 15]. In the case of a STM, one electrode is the tip while the other is the sample. A potential difference is applied and the tip is scanned over the surface of the sample with a small gap between the tip and the sample (less than 10 nm) [4]. Since the tunneling current is proportional to the gap width, height variations result in tunneling current variations since the tip stays at constant height. This technique requires a conducting tip and sample. The tip is therefore metallic and needs to be very sharp. Most non-conducting surfaces can also be scanned with an STM after being coated with a thin layer of conductive material [4, 6, 10, 11, 15]. Although the STM has some specific requirements which makes it not suitable for all types of surfaces, its high sensitivity to small height variations makes it a very useful instrument, *inter alia*, to measure the surface roughness at the nanoscale of conductive samples.

Atomic Force Microscopy on the other hand does not require a conductive tip nor surface. Nevertheless, its vertical and lateral resolution are on the order of 0.1 nm [4, 15]. AFM measures the interaction forces between the tip and the surface (less than 1 nN). Like for the STM, the tip is scanned over the surface but, in contrast to the STM, the total interaction force between the tip and the surface determines the height variations of the sample instead of the tunneling current. AFM can be used in three different modes: the contact mode where the tip is constantly in contact with the sample (as for the stylus profiler), the intermittent-contact mode or tapping mode and the non-contact mode where the tip only approaches the surface but never touches it [4, 6, 10, 15]. AFM was used during this study to evaluate the roughness of the fibers of the fabrics. A more detailed explanation of its working principle and running parameters is given in section 2.4.

Other methods

Additionally to the most used methods and instruments already presented, other more or less common methods exist to evaluate surface roughness.

Fluid methods such as the hydraulic method or pneumatic gauging method are two techniques that are usually used for quality control procedures. Roughness is determined empirically from the numerical data [4].

The capacitance method is a possible electrical method. Based on the parallel capacitor principle, the sample surface is considered as the sum of a small areas of different heights. The capacitance between a smooth disk and sample surface, which is a function of the roughness, is measured. This capacitance is proportional to the area of the surfaces and the dielectric constant of the medium, but inversely proportional to the distance that separates the two electrodes. The capacitance is then measured for all the

small surfaces and differences in their magnitude are due to the surface roughness which alters the distance separating both surfaces. Nevertheless, this method requires both surfaces to be conductive [4, 11].

Scannening Electron Microscopy method can also reveal micro and macroscopic features of surfaces. However, it is hard to obtain quantitative data to calculate the roughness. As for previously mentioned methods, the surface needs to be conductive too. Non-conductive surfaces can be coated if needed [4].

To sum up, there are different possibilities to measure surface roughness. The choice of the used technique depends on the sample but also on the requirements of the instrument. Table 1.1 provides a comparison between the most often used techniques to measure surface roughness and that have been described in this section.

Method	Quantitative information	Three-dimensional data	Lateral resolution (nm)	Vertical resolution (nm)	Comments
Stylus profilometry	Yes	Yes	15-100	0.1-1	Lateral resolution is dependent on the radius tip. Direct contact with the sample can cause damage to the surface. 3D mapping is time consuming.
Optical interference	Yes	Yes	500-1000	0.1-1	High vertical resolution even for very rough surfaces and no direct contact with the sample.
STM	Yes	Yes	0.2	0.02	Conductive surfaces are required and a only small areas can be scanned (for micro or nano roughness features).
AFM	Yes	Yes	0.2-1	0.02	No requirements for the analyzed sample and only small areas can be scanned (for micro or nano roughness features).
Electron microscopy	Yes	Yes	0.2-1	0.02	Conductive surfaces are required and only small areas can be scanned. Measurements are performed under vacuum (not possible for all samples) and the data is limited.

Table 1.1 – Comparison of the characteristics of the different techniques used to measure the surface roughness that are described in this section. This table is adapted from the book by B. Bhushan [4].

1.2 Hydrophobic properties of fabrics

Being cold because of wet clothes is a feeling everyone has experienced and one of the main objectives of textile industry is to provide protection to water through clothes but also other types of outdoor equipments and products. Therefore, one needs fabrics that repel water, in other words, hydrophobic fabrics (*hydro* stands for water and *phobos* for fear in Greek). A surface exhibiting a static contact angle larger than 90° is classified as hydrophobic and as superhydrophobic if the contact angle exceeds *ca.* 150° . More generally, the contact angle is a quantitative parameter describing the wetting properties of a solid surface for a given liquid [16–18]. Geometrically speaking, the contact angle of a liquid on a solid substrate is the angle defined between the surface of the solid and the tangent to the water droplet at the triple line, i.e. the line where the liquid, solid and gas state intersect (Figure 1.3). The higher the contact angle, the more the solid repels water.

Hydrophobic properties for textiles are thus very interesting to provide water protection. The range of applications of hydrophobic fabrics goes from simple rain protective coats to military and medical equipment [19]. The wide field of use led to intensive research to first understand the physics behind the phenomenon of hydrophobicity and then use this property for commercial and professional applications. Numerous examples of hydrophobic surfaces can be found in nature which helped scientists to study this phenomenon. The most well-known example is probably the lotus leaf and its self-cleaning property called "the lotus effect" [17, 18, 20]. Studying this plant revealed that surface roughness and surface energy are the two major parameters affecting the wettability of a solid surface. Since surface energy is modified in this study by depositing coatings on the fabrics, we discuss the requirements of these coatings to give or enhance hydrophobic properties to fabrics at the end of this section. Before that, one needs to understand more deeply the interaction of water and, even more generally, of liquids with a solid surface.

1.2.1 Surface-water interaction

As previously explained, the contact angle quantifies the wettability of a solid surface regarding a given liquid. The value of the contact angle (Figure 1.3) measured in static mode with water, allows to characterize the wettability of a solid surface. For instance, if the water droplet tends towards a spherical shape when it is in contact with the solid surface, one can conclude that the surface is water-repellent. The shape adopted by the liquid droplet is caused by the interactions of the molecules at the solid-liquid interface. The resultant of forces at the liquid surface is different from zero because molecules at the interface experience attractive forces from surrounding molecules. A net force is applied to them since they are not surrounded by the same type of molecules [16–18, 20]. Indeed, air molecules as well as water and surface molecules interact with the molecules at the surface of the water droplet. At the air-liquid interface, the attraction between water molecules is larger than the one between water and air molecules, resulting in an inward net force applied to the water molecules at the air-liquid interface. This net force applied

to the water molecules at the interface is called surface tension and reflects the cohesion of the underlying phase. The inward net force applied at the air-liquid interface is an unbalanced force thermodynamically unfavorable. Hence, the liquid seeks to minimize its surface area to decrease the inward pressure caused by this inward net force. To do so, the water droplet tends to adopt a spherical shape at the air-liquid interface.

Thermodynamics will also dictate the behaviour of a liquid deposited onto a solid surface. As for the liquid, the solid also has a defined surface energy (energy per unit area) or, in other words, a force per unit length (surface tension). Therefore, the higher the solid surface energy, the higher the attractive force applied to the water molecules [16–18, 20, 21]. One can understand from this thermodynamical approach that the lower the surface energy of the solid surface is, the less the liquid wets the solid surface. For solid surfaces that do not exhibit hydrophobic properties one needs to reduce their surface energy to achieve water repellency. One way of altering the wettability of solid surfaces is to treat them chemically by depositing other molecules with their own wetting properties onto the surface. Dip-coated fabrics, as studied in this work, is one example of chemical treatment.

Young-Dupré equation

For a given solid surface energy, three surface tensions coexist at the three-phase boundary. To maintain the shape of the liquid droplet, the system must be at static equilibrium, i.e. the three surface tensions apply together a net force equal to zero at the three-phase boundary. If one consider a water droplet on an ideal surface (completely flat and chemically homogeneous), the equilibrium at the solid-liquid-vapor interface can be described by equation 1.11. γ_{sv} , γ_{sl} and γ_{lv} are the surface tensions of the solid-vapor, solid-liquid and liquid-vapor interface, respectively. The contact angle for an ideal surface at the three-phase intersection is denoted by θ_Y and is referred to as the Young-Dupré contact angle. Equation 1.12 on the other hand, is a rearrangement of equation 1.11 and is referred to as the Young-Dupré law [22]. From this law, it is possible to predict the contact angle of a solid surface. Yet, these equations are only valid for an ideal surface. Hence, contact angles measured for experiments on rough surfaces can be very different to the one predicted by Young-Dupré equation [16–18, 20–23]. Two main theories, namely the Wenzel and the Cassie-Baxter models, further describe the behaviour of the contact angle for non-ideal surfaces.

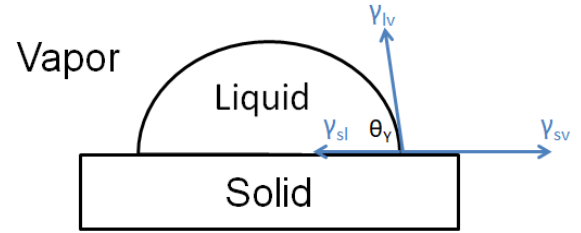


Figure 1.3 – Schematic of Young-Dupré equation with the different surface tensions applied at the three-phase boundary and the measured contact angle (θ_Y).

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta_Y \quad (1.11)$$

$$\cos \theta_Y = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (1.12)$$

Wenzel model

In addition to the effect of surface energy, Wenzel considered the surface roughness and described how it affects the measured contact angle. To do so, the water droplet is assumed to fully penetrate the space between the roughness grooves, i.e., the solid surface under the water droplet is homogeneously wetted (Figure 1.4a). The roughness scale is assumed to be much smaller than the water droplet size. Moreover, the surface is still considered as chemically uniform [1, 17, 18]. Wenzel introduced a geometrical factor called the roughness factor (r) to describe the surface roughness as already mentioned in section 1.1.1 (see equation 1.1). This factor is the ratio of the real surface area to the projected surface area and is consequently equal to 1 for a completely smooth surface and increases with increasing roughness.

A rough surface increases the contact area by factor r compared to a smooth surface according to Wenzel definition of the roughness factor. As a consequence, the surface energies of the solid-liquid and solid-vapor interface are also increased by a factor r . If one applies these considerations to equation 1.12, one gets the following equation given by Wenzel [1]:

$$\cos \theta_W = \frac{r \times (\gamma_{sv} - \gamma_{sl})}{\gamma_{lv}} = r \cos \theta_Y \quad (1.13)$$

where θ_W is the apparent contact angle and θ_Y the contact angle according to Young-Dupré equation. The relationship between the apparent contact angle (θ_W) and the intrinsic contact angle (θ_Y) given by Wenzel, highlights the interdependence of surface energy and surface roughness. Indeed, the roughness reinforces the underlying wetting properties of the surface. For both hydrophilic and hydrophobic surfaces, the introduction of roughness reinforces the existing wettability of the surface. If $\theta_Y < 90^\circ$ (hydrophilic solid surface) and $r > 1$, θ_W is always smaller than θ_Y . Likewise, if $\theta_Y > 90^\circ$ (hydrophobic solid surface) and $r > 1$, θ_W is always greater than θ_Y and the surface thus repels water even more for an increasing roughness. As a result of this equation, surface energy and surface roughness have always to be considered together if a high water repellency is wanted [1, 16–18, 20, 23].

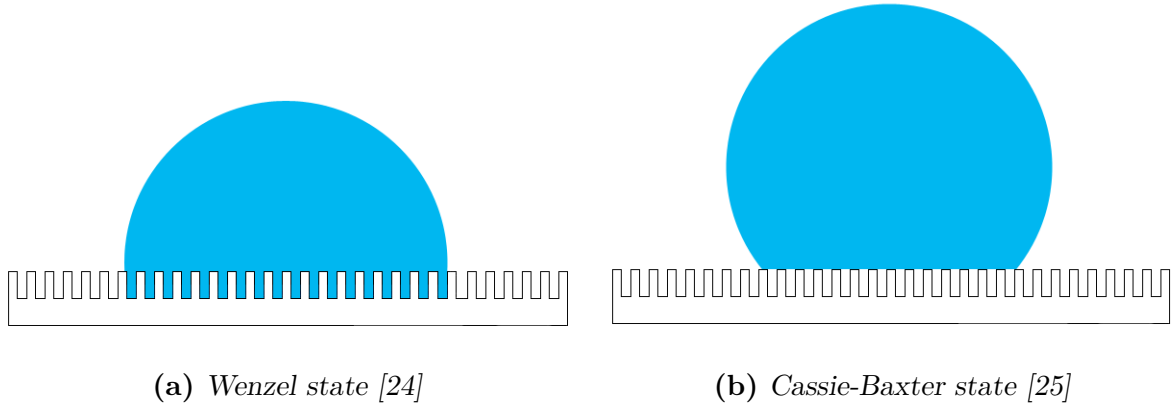


Figure 1.4 – *Illustration of the Wenzel state where the roughness grooves are filled with water (homogeneously wetted surface) compared to the Cassie-Baxter model where air-pockets are trapped in the grooves under the water droplet.*

Cassie-Baxter model

Cassie and Baxter held the same type of reasoning as Wenzel except they considered a planar but chemically heterogeneous surface, i.e., having different local material compositions [16–18, 26]. The local surface areas of different materials are assumed to be very small compared to the droplet size. The simplest scenario of the Cassie-Baxter regime is to consider that the surface is composed of two different materials as shown in Figure 1.4b (in this figure the second material is air). The next step is to assume each species have their own contact angle, θ_1 and θ_2 , respectively. The fractional surface areas of each material are denoted as f_1 and f_2 where $f_1 + f_2 = 1$ [26]. The measured contact angle (θ_{CB}) in this regime is in-between the two contact angles of both materials as one can deduce from the following equation:

$$\cos \theta_{CB} = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (1.14)$$

In the case the second material is air trapped in the grooves (forming air-pockets), equation 1.14 can be simplified. To do so, one assumes the liquid-vapor fraction f_{lv} to have a contact angle of 180° . On the other hand, the solid-liquid fraction f_{sl} is assumed to have a contact angle of θ_Y (Young-Dupré contact angle, equation 1.12), i.e. the contact angle that would be measured on a completely flat surface with the same surface energy as the considered solid surface [16–18, 20]. The equation then becomes:

$$\cos \theta_{CB} = f_{sl} \cos \theta_Y - f_{lv} = f_{sl} \cos \theta_Y - (1 - f_{sl}) \quad (1.15)$$

The conclusions arising from equation 1.15 are different than the ones from Wenzel relationship. Indeed, surfaces in Cassie-Baxter regime can exhibit hydrophobic properties despite an intrinsic contact angle (θ_Y) lower than 90° what is impossible according to the Wenzel model. For this reason, surfaces exhibiting the Cassie-Baxter regime are favoured to achieve superhydrophobicity ($\theta > 150^\circ$). Moreover, to maximize the contact angle θ_{CB} ,

the surface area of the solid-liquid interface should be minimized. In contrast to the Wenzel model, a theoretical contact angle of 180° can never be reached since it would require $f_{sl} = 0$ or $\theta_Y = 180^\circ$, which is in both cases physically impossible [16–18, 20, 23, 26].

Wetting transitions

The Cassie-Baxter regime considers the solid surface to be flat but equation 1.15 can be modified introducing the roughness factor defined by Wenzel. Though air trapped underneath the water droplet even further increases hydrophobicity, the thermodynamical stability of this regime must be assessed too. The energetically favoured state (between the Wenzel and Cassie-Baxter state) can be predicted if one assumes the transition between both states to occur at a critical contact angle θ_c that shows the same value as θ_W and θ_{CB} . Equaling equations 1.13 and 1.15 allows to determine this critical angle (equation 1.16).

$$\cos \theta_c = \frac{1 - f_{sl}}{r - f_{sl}} \quad (1.16)$$

The Wenzel state will be favourable when $90^\circ < \theta_Y < \theta_c$ while the Cassie-Baxter regime will be favourable when $\theta_Y > \theta_c$. From equation 1.16, we can conclude that θ_c is always larger than 90° if the surface is rough since $r > 1 > f_{sl}$. Nonetheless, experiments showed that air-trapping could occur even in the stability region of the Wenzel state. The existence of a meta-stable Cassie-Baxter state was thus highlighted through these experiments [16–18, 20].

1.2.2 Coatings to get hydrophobic properties

It is now clear that to get fabrics exhibiting water repellent properties, the fabric surface needs to show a low surface energy. If so, increasing the surface roughness would then increase the wetting behaviour of the fabric (section 1.2.1). On the one hand, most fabrics have a surface energy that does not allow them to show hydrophobic properties. On the other hand, textiles do present an inherent macroscopic roughness. This is mainly due to the weave pattern and the yarns and loose fibers that stick out from the surface resulting in height differences at the surface of the fabric. Moreover, roughness features on fibers can also be expected at the microscopic scale. Consequently, starting with the modification of the surface energy alone could already substantially change the wettability of the fabrics [17, 27].

Changing the surface energy can only be done by changing the chemical properties of the surface. Chemical treatments are thus required and one possibility is to coat the surface with a thin layer of chemical agents of low surface tension (as done in this study) [17, 19, 21, 27, 28]. This technique is one of the most widely used because it is easy to perform. The production process is flexible which has led to the development of different wet and chemical vapor deposition treatments [17]. The used compounds are usually

fluorinated compounds, hydrocarbons, polyurethanes and polysiloxanes which can provide materials, such as textiles, hydrophobic properties [17, 19, 29]. Further modifications to the surface, as altering the roughness at nano or micro scale, are possible in order to achieve specific wetting characteristics [27]. Yet, this study only focuses on the influence of the intrinsic fabrics roughness to assess the wetting properties after coating them with chemical agents that are specified in section 2.2.1.

Drawbacks and problems of current coatings

As for any industrial process, safety and durability are two major parameters in the choice of chemical agents for coatings. These aspects have to be considered together with the final performances. Risks for the human health or the environment are also part of the balance and have to be taken into account when designing effective coatings. For the past few years, C8-fluorocarbons have been widely used due to their high water and oil-repellent properties [17, 19, 30, 31].

C8-fluoropolymers/fluorocarbons designate the set of polymers having side chains consisting of eight carbon atoms covalently bonded to at least two fluorine atoms. More generally, perfluoroalkyls and polyfluoroalkyls designate the family of polymers containing a (part of) carbon chain of chemical composition C_nF_{2n+1} . The acronym PFAS is used to refer to this family of polymers [31]. The C-F bond makes these chemicals very interesting since it is very strong and stable (both chemically and thermally). Moreover, this specific covalent bond has a hydrophobic and lipophobic nature and is therefore very attractive to prepare hydrophobic and even oleophobic coatings. The longer the fluorinated chain, the more the hydrophobic and lipophobic properties are enhanced [31]. Therefore, long-chain fluorochemicals, usually containing eight carbon atoms (hence the terms C8-chemistry, C8-fluorocarbons,...), have been widely used in applications where such properties could be useful [6, 27, 31–33].

Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are two chemicals formed after degradation of C8-fluoropolymers used for coatings. Recently, several studies reported that these substances are bioaccumulative, persistent in the environment and dangerous for the aquatic organisms which are on the front line of the pollution chain. Moreover, it was showed that these chemicals present a risk for human health (inducing low fertility, cancer and damage to the immune system) [27, 30–35]. These severe issues with PFAS led governmental authorities to take actions. For instance, the European commission decided to forbid PFAO and derivatives starting from 2020 on, at least in most fields of applications, and from 2032 for medical devices [36]. The United States Environmental Protection Agency (EPA), on the other hand, also took a series of regulatory actions to deal with this issue [37]. Since C8-fluorocarbons showed the best properties compared to other possible coatings, these compounds were widely in the industrial sector and they can be found in numbers of daily applications [19, 32, 34].

However, because of the environmental and health issues they present, researchers need to find alternatives and, if possible, without losing performances compared to the current coatings.

Possible solutions or strategies

The legal framework introduced for C8-chemicals forced scientists to find alternatives. Because of the unique properties of the C-F bond, the first considered solution was C4-C6 fluoroalkyl chemistry since they are the closest chemically to C8 compounds [32, 38]. There is a loss of performance with this alternative since reducing the length of the polyfluoroalkylated side chains in PFAS reduces the water and oil repellency [39]. However, shorter perfluorinated chains result in less persistent, bioaccumulative and toxic byproducts but even for fluorocarbons of shorter chain length, it seems that the risks for the environment and the human health are important too [30, 33]. Therefore, one can presume that these chemicals will be restricted in the future as well. Though C4-C6 provide a short term solution, the need of greener chemicals and new technologies for water repellent coatings is crucial. [32, 34, 40].

The real challenge is to develop coatings that show both hydrophobicity and oleophobicity. Water repellent chemicals only are easier to find. Since water is a polar molecule, using apolar chemicals contribute to prevent wetting. On the other hand, lipids and oil are apolar molecules that have very low surface tensions so these same apolar chemicals would not provide oil repellency while PFAS do repel both types. Existing alternatives to fluoropolymers such as silicone derivatives and polydimethylsiloxane (PDMS) can provide water repellency but hardly oil repellency [41]. Hydrocarbons (apolar molecules) also provide good water repellency but then again, they cannot achieve oil repellency [30]. One promising technology to achieve both oil and water repellency is maybe the dendrimer technology [30, 33, 39, 40].

Dendrimers are highly branched monomers with symmetric branching units around a core molecule [30, 33, 40]. They can carry many functional groups which will influence their properties. The regular and compact shape of dendrimers allows them to incorporate guest molecules and have therefore unique properties. Combined with fluorocarbons, dendrimers could provide oil repellency and sometimes even more efficient water repellency. Furthermore, the amount of fluorochemicals used in these cases are lower compared to non-dendrimer finishes. Industrial dendrimer-based products are nowadays available for the production of water-repellent coatings and research is going on to further explore this possibility [30, 33, 40].

Actually, the evolution of the legal framework led manufacturers (including the textile industry) to reconsider the specifications of their products. The question is: must the product truly be water and oil-repellent simultaneously? It seems that for most of the products, water repellency is a necessity while oil repellency may be considered as an

additional and interesting feature. On the other hand, the products on the market of the last decades that showed water and oil repellency might have led some consumers to accustomed to have both properties at the same time. Therefore, customers might expect the products to have these two properties even on future products. Providing these characteristics to products was possible with fluorocarbons but the costs and difficulties to achieve it with other chemical compounds forced industrial companies to set their priorities. Based on the industrially available and legal chemical products to prepare coatings, it seems that in the near future, customers will not be able to buy many items showing oil and water repellency. However, this might rapidly change if a new technology that is cost effective, human and environment friendly appears on the market.

1.3 Weave types for fabrics

Fabrics can have different types of weaves. The fabrics we used in this study show two different types of weaves which are detailed here. However, before explaining the two types of weaves, it is useful to elucidate the difference between warp yarns and weft yarns. On the one hand, warp yarns refer to the longitudinal threads that are stationary and attached to a loom (weaving frame). On the other hand, weft yarns are the threads that alternatively pass over and under the warp yarns to form the weave. Figure 1.5a illustrates the difference between these two threads.

The difference in the two types of weaves encountered for the used fabrics, resides in how the weft yarns are inserted between the warp yarns. The fabrics that were used in this study are detailed in section 2.1.

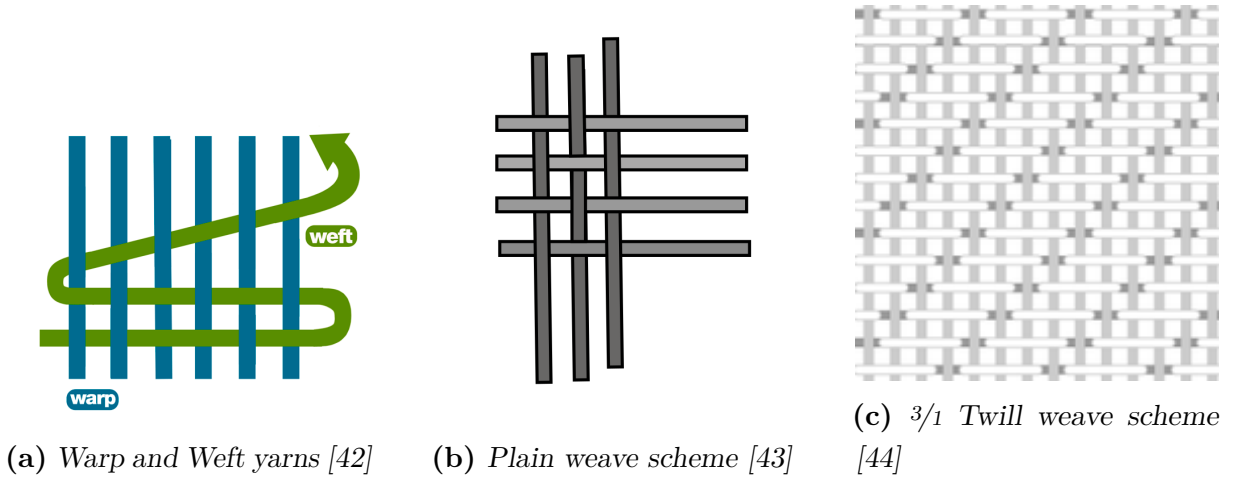


Figure 1.5 – The two different types of yarns, (a), and the types of weaves involved for the fabric samples (b and c).

Plain weave

In the case of a plain weave, the weft yarns are alternatively passed over and under the warp yarns along the full length of the fabric. Both yarns cross at right angles and thus a basic cross pattern is obtained (Figure 1.5b).

Twill weave

Concerning the twill type, the weft yarn passes over two or more warp yarns before passing under one or more warp threads, and so on. Additionally, between each row, a shift is added to the sequence of the weft yarn passage above and under the warp yarns. This results in a pattern of parallel weft yarns that stick out on a diagonal (Figure 1.5c).

Chapter 2

Methods and instruments

This section details the characteristics of the different fabrics that were used in this study as well as the coatings we applied to their surfaces. Their respective features and properties are described and the procedure to apply the coating to the different samples is further developed.

Moreover, different instruments were used to characterize our samples and provide us with specific data, namely a stylus profiler, an Atomic Force Microscope (AFM) and a contact angle apparatus. For all these techniques, the important feature(s) that can be extracted from the measured data are tackled in addition to their working principles and the parameters used to perform the measurements.

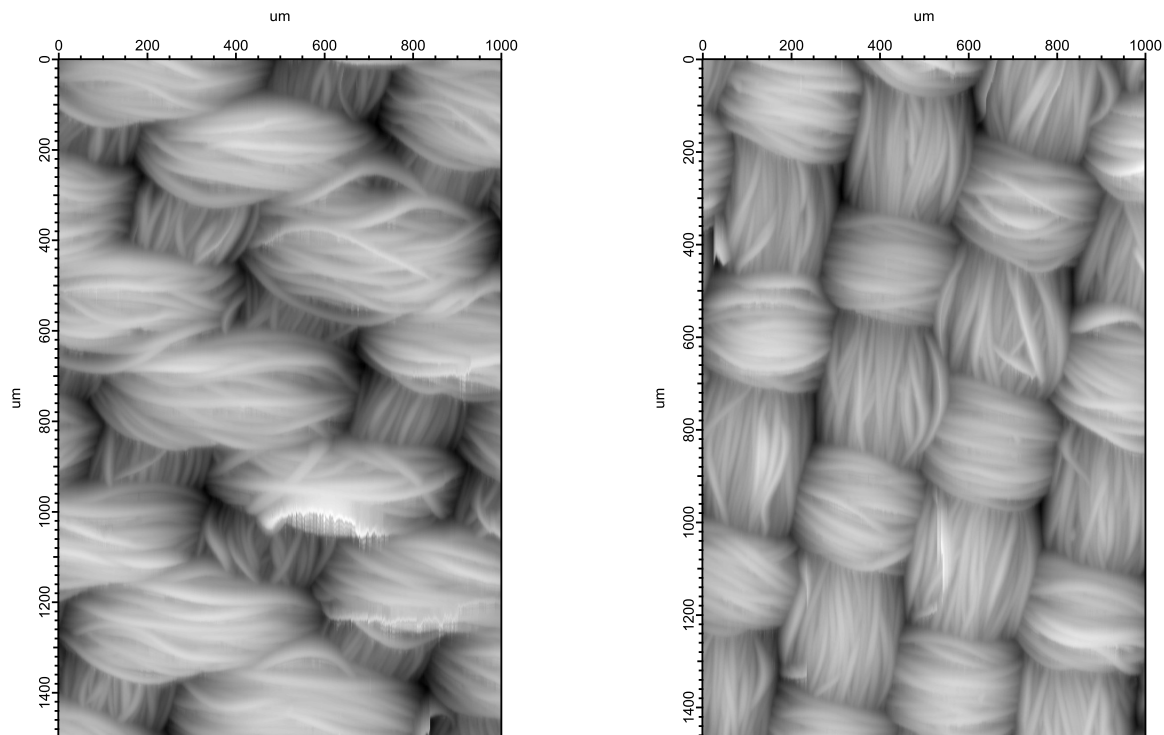
2.1 Polyester fabrics

The fabrics for this study were all woven synthetic polyesters with a varying surface roughness (Table 2.1). The choice of these fabrics was done in order to cover a large range of roughnesses. Having such different roughnesses offers the possibility to analyze how the hydrophobic properties evolve with an increasing fabric roughness for a given coating. Seven different fabrics were used which are listed in Table 2.1. One way of describing the roughness of the fabrics is to use the roughness factor r defined by Wenzel (equation 1.1). The covered range of roughness goes from $r = 1.2$ to $r = 1.85$. These results are discussed and further detailed in section 3.1.1. In addition to the fabrics, silicon wafers were coated. The purpose was to make the same surface measurements as for the fabrics but on a flat model surface, i.e., a surface with a roughness of 1. These last measurements provided us with the contact angle θ_Y , defined by Young-Dupré in equation 1.12.

Name	Type	Supplier
Fabric1	plain	Decathlon
Fabric2	plain	Centexbel
Fabric3	plain	Decathlon
Fabric4	plain	Decathlon
Fabric5	plain	Centexbel
Fabric6	plain	Centexbel
Fabric7	twill/plain	Centexbel
Single-side-polished (100) silicon wafers	flat surface	TOPSIL

Table 2.1 – *List of the fabrics used in this study along with their type of weave and the supplier. The Fabric7 sample has two different faces, one of them has a twill weave (Figure 2.1a) while the other side is closer to a plain weave (Figure 2.1b). The silicon wafers were used to do the same measurements as for the fabrics but on a flat surface.*

All the fabrics used in this study were woven and different types of weave patterns can be produced. In our case, all of them showed a plain weave on both sides except for the Fabric7 sample. On one of its sides, a twill weave is observed while on the other, a weave pattern very close to a plain weave is observed. This fabric provided two different measurements depending on the side that was scanned. Therefore, each side was considered as a different sample. In the end, one could say that eight samples were used but only seven different fabrics provided. For the side of the Fabric7 sample that exhibits a twill weave, the pattern drawn by the warp and weft yarns is referred to as a $2/1$ twill weave (Figure 2.1a). The specific case of the Fabric7 sample is discussed more deeply in section 3.1.4.



(a) *Fabric7 2/1 twill side which is called: face A*

(b) *Fabric7 plain side which is called: face B*

Figure 2.1 – *Illustration of the two different sides of the Fabric7 sample.*

2.2 Sample coatings and coating procedure

This section focuses on the coatings used to provide to the fabrics hydrophobic properties as well as the procedure to apply them onto the fabric surface. The chemicals used provide a low surface energy to the fabrics and therefore, water-repellent properties.

2.2.1 Three different coating formulations

Three different coatings have been studied in parallel and the information about the three commercial formulations used to prepare them are provided in Table 2.2. For the rest of this report, the name mentioned in the column "*given name*" will be used when referring to the coatings prepared from these commercial formulations.

The formulation "WACKER® HC 303" is an extremely finely dispersed water-based silicone emulsion with ~ 17 wt% solid content. The size of the particles in this suspension is in the nanometer range.

The second formulation "3M™ Protective Material PM-900" is a water-based emulsion containing a C4-fluoropolymer (polyurethane containing perfluoroalkyl chains of four carbon atoms) with ~ 30 wt% solids.

Finally, the product "Schoeller Protec FF" is a dispersion of paraffin oils and a fat modified melamine resin which is nonionic/cationic in nature.

Product Name	Supplier	Given name
WACKER® HC 303	Wacker	PDMS
3M™ Protective Material PM-900	3M	PM900
Schoeller Protec FF	Schoeller Technologies AG	SchPFF

Table 2.2 – *The three formulations used in this study to prepare the hydrophobic coatings that were deposited on the fabrics. For the rest of the report, the "given name" will be used when referring to the coatings prepared from these formulations.*

2.2.2 Coating procedure

The coating procedure was the same for each type of formulation and sample, except for the silicon wafers for which it is discussed in section 2.2.3. All fabrics were dip-coated in a solution of the commercial formulation diluted with Milli-Q water (resistivity 18.2 MΩ.cm, obtained from a Merck Millipore system, Milli-Q® Reference). The final concentrations of the formulations used to prepare the hydrophobic coatings are provided in Table 2.3. The coating procedure consists of two main steps to ensure the deposition and cross-linking of the coating. The first step consists of dipping a piece of fabric in the prepared solution. The sample is immersed in the suspension for three minutes. Then the piece of fabric is removed and placed on a hot plate which is at $\sim 150^\circ\text{C}$ for two minutes to perform annealing. This annealing step has as purpose to fix the coating on the sample surface but also to trigger the cross-linking between the different molecules of the coating. Once the annealing step is over, the samples are ready to be studied.

Coating	Formulation concentration (wt%)	Dipping time (min)	Annealing time (min)
PDMS	~ 1.5	3	2
PM900	~ 1.5	3	2
SchPFF	~ 8	3	2

Table 2.3 – *Description of the conditions used to deposit the hydrophobic coatings on the fabrics.*

2.2.3 Silicon wafer coating procedure

Silicon wafers on the other hand cannot be coated by dip-coating, and suspensions with different concentrations were necessary. In order to apply the coating onto such a flat surface, we used a spin coater, i.e., the coating was applied by spin-coating. To do so, a piece of silicon wafer is first placed at the center of the spin coater. A given volume of suspension is then poured on the wafer before closing the spin coater. Afterwards, the angular speed and time of rotation are set to control the thickness of the resulting coating. The angular speed is one of the parameters that affects the thickness of the resulting

coating. Of course, other parameters also influence the film thickness, such as the viscosity of the solution and its concentration.

For the deposition of the three coatings studied in this work, the angular speed was set to 3000 rpm for 30 s. Moreover, the time to achieve the maximum rotation speed was set to 5 s. As mentioned previously, the concentrations of the suspensions to coat the silicon wafer were different compared to the fabric coating procedure. For the silicon wafers, the PDMS solution was used as provided, i.e., with ~ 17 wt% of solid particles. Regarding the PM900 and the SchPFF, their concentrations were decreased by a factor of two by diluting them with Milli-Q water. Finally, once spin-coated, the same annealing procedure as for the fabrics took place. The silicon wafers were thus annealed for two minutes on a hot plate at $\sim 150^\circ\text{C}$.

2.3 Measurement of the macroscopic roughness by stylus profilometry

The importance and the role that the roughness plays in the final hydrophobic properties has been acknowledged in section 1.1 and 1.2.1. The first step was to evaluate the macroscopic roughness of the sample. To do so, a stylus profiler was used, the DektakXT from Bruker. This technique provides a step-height measurement with a repeatability of $5\text{ \AA}$ [45] and does not require any specific properties from the sample surface. Stylus profilometry offers both high vertical and lateral resolution (at the macroscale). The profilometry measurements were performed on the different fabrics, before and after deposition of the coatings.

To determine the macroscopic roughness on a delimited area of the fabric, one needs to use the 3D mapping option of the stylus profilometer. The out-coming data is then a three-dimensional scan of the measured area. The treatment of the data obtained by 3D scanning of the surface allowed us to compute the roughness factor for each sample surface (see section 3.1).

2.3.1 Principle of profilometry

The stylus of the profiler is equipped with a diamond tip ($0.7\text{ }\mu\text{m}$ radius) at its extremity. This tip is moved across the sample surface in the y axis direction for a specific scan length, scan speed and contact force. When the scan length is completed, a single line scan (trace) is performed. During the tip displacement, a constant force is applied between the tip and the surface. We considered the sample surfaces to be homogeneous and therefore, only height variations can cause the interaction force to change. To maintain the stylus force on the surface constant, the tip is moved vertically (z axis) thanks to a feedback loop while the height variation signal of the tip is recorded.

The 3D mapping option has a similar working principle compared to a simple line scan. Nevertheless, one additional parameter is involved which is the distance (x axis) between each adjacent line scan or trace. Each time a new trace starts, its starting position is shifted by a distance chosen by the user. At the end of the 3D scan, the traces are assembled together to form a 3D image of the surface. We then have a height variation signal in the y direction from each line scan but in the x direction as well because all the adjacent traces have been assembled to form a single image. The data to be treated is thus a matrix for which each point has x, y and $z(x, y)$ coordinates.

2.3.2 Parameters used for profilometry measurements

Other parameters as the ones already mentioned are to be adjusted to launch the 3D scan of a surface and these are gathered in Table 2.4. All scans were performed with the same parameters. The adjustment and the importance of each parameter are discussed in section 3.1.5.

Range:	524 μm	Mode:	Valleys
Stylus force:	1 mg	Length:	2000 μm
Map extend:	1000 μm	Duration:	7 s
Map resolution:	2 μm	Resolution:	0.951 $\mu\text{m}/\text{pt}$
Traces:	500	Points:	2101
Stylus Radius	0.7 μm	Speed:	285.714 $\mu\text{m}/\text{s}$

Table 2.4 – Parameters used to perform stylus profilometry measurements. The **range** is the maximum height variation of the stylus tip. The **mode** parameter can be set to 'hills', 'valleys' and 'hills and valleys'. The used mode determines which part of the signal is recorded. Points below (valleys) or above (hills) a zero height level (defined by the instrument) are recorded. Points above (valleys) or below (hills) this specific level see their height assigned to the maximum (valleys) or minimum (hills) possible height. The mode 'hills and valleys' combines both and records the data points that are below and above the zero height level. The **map extend** is the size of the scan in the x axis direction. The **duration** is the time imposed to the tip to travel the scan **length**. The **map resolution** is the distance in the x axis direction between each trace, in other words, the lateral resolution. The **traces** parameter is the number of line scans performed per 3D scan. The **points** parameter is the number of points recorded per line scan.

2.4 Measurements of the fiber roughness by Atomic Force Microscopy

Atomic Force Microscopy (AFM) was used to measure the fiber roughness of the different fabrics. On the one hand, the macroscopic roughness due to the combination and arrangement of the polyester fibers was determined by the stylus profiler as explained just above. On the other hand, a microscopic roughness at the surface of the fibers also exists and needs to be determined. The AFM is the appropriate tool for such a measurement because of its high resolution at the nanometer scale and it does not require the sample to have any specific properties as summarized in Table 1.1. Since the total surface roughness is the combination of the macroscopic and microscopic roughness, we needed to evaluate the microscale features at the surface of the fibers and their influence on the total roughness.

The AFM used for these measurement was an ICON Dimension from Bruker and we worked under ambient air conditions. The cantilever used for these experiments was purchased from *NanoAndMore GMBH*, of the brand Nanosensors and the model was PPP-NCHR. These tips have a standard shape and a radius of less than $10\text{ }\mu\text{m}$. The cantilever has a resonance frequency of 330 kHz , a force constant of 42 N m^{-1} and a length of $125\text{ }\mu\text{m}$ (nominal values).

2.4.1 Principle of Atomic Force Microscopy

AFM is a Scanning Probe Microscopy technique in which the force acting on the tip approaching the surface results in the deflection of the cantilever which is measured by an optical system. The deflection of the cantilever is proportional to the measured force which allows the device to estimate the force applied on the cantilever at any given position. The AFM has a few main components: the laser beam, the cantilever with a tip at its end, the piezo-electric scanner (PZT) and the photodiode detector (PDD) as shown in Figure 2.2.

When a sample is scanned, the tip interacts with the surface and is subject to adhesive and repulsive forces. The sum of all the forces acting on the tip results in a certain deflection of the cantilever for each data point of the scanned area. The deflection of the cantilever is thus a measurement of the total force applied on the tip when interacting with the surface. The laser beam that strikes the cantilever is reflected onto a PDD. As can be seen in Figure 2.2, the position of the reflected beam on the PDD is proportional to the cantilever deflection. Thanks to a calibration step of the cantilever and the PDD performed before starting the measurements, the position of the laser beam on the PDD when the tip is not subject to external forces from the sample is known. Therefore, while scanning the sample, the reflected laser beam position on the PDD is a function of the net force applied to the tip.

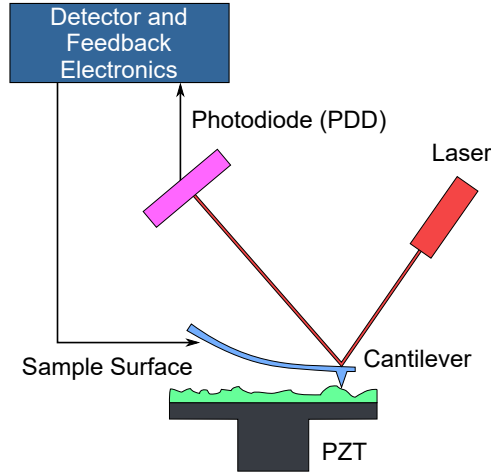


Figure 2.2 – Scheme regrouping the major components of an AFM: the laser beam, the cantilever with the tip at its end, the piezo-electric scanner (PZT) and the photodiode detector (PDD) [46].

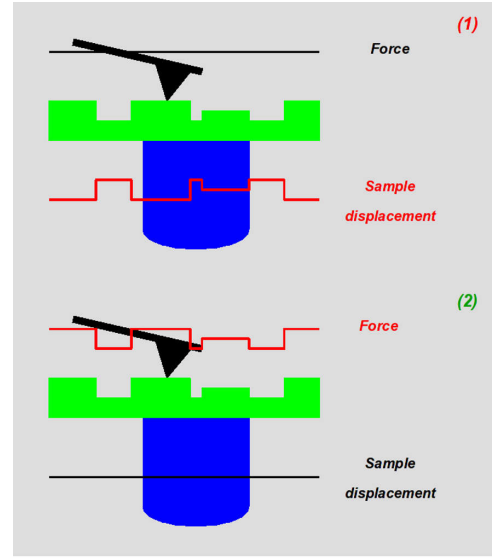


Figure 2.3 – The two possible working modes of an AFM: the constant force mode (1) and the constant height mode (2) [15].

The relation between the force measurement and an image of the topography of the surface still needs to be done. However, this requires to specify which type of working mode has been chosen. There are two possibilities, constant height or constant force measurement as shown in Figure 2.3. In the case of constant height working mode, the tip stays at a determined height and measures the variation of the force on the tip as a function of the sample displacement. The force signal is then treated by the software in order to provide a topographical image of the surface. On the other hand, the constant force working mode, which was the one used in this study, uses a feedback loop to adjust the tip or sample height so that the force between the tip and the surface remains constant. The signal of the sample or tip displacement is then used by the software to generate the topography of the scanned area.

Finally, for the analysis of our polyester fabrics by AFM, before and after coating, an intermittent contact mode or tapping mode was used. In the case of tapping mode, the cantilever oscillates up and down close to its resonance frequency. The amplitude and frequency are kept constant by the help of the feedback loop. When the tip approaches the surface, the interaction forces result in the alteration of the amplitude. The amplitude signal is used by the software to adjust the cantilever height to maintain a constant force between the tip and the surface, so that the amplitude of oscillation of the cantilever also remains constant. The adjustments made to keep the amplitude constant are recorded and used to generate the topographical image.

2.4.2 Parameters used for AFM measurements

The parameters used to perform the AFM measurements are listed in Table 2.5. The adjustment and the justification for these parameters are detailed further in section 3.2.4. For each sample two scan sizes were performed: $8 \times 8 \mu\text{m}^2$ and $3 \times 3 \mu\text{m}^2$ and this at four different places on the sample surface to ensure a repeatability of the results.

Scan size:	8×8 and $3 \times 3 \mu\text{m}^2$	Integral gain:	Variable
Scan rate:	0.75 or 1 Hz	Proportional gain:	5
Sampling points/line:	256	Amplitude setpoint:	Variable (mV)
Number of lines:	256		

Table 2.5 – Parameters used to perform AFM measurements. The **scan rate** is the frequency at which the tip travels each line scan. The **sampling points/line** parameter refers to the number of sampling points recorded per line scan. The **number of lines** parameter sets the number of parallel line scans performed along the height of the scan since the tip travels horizontally. The values for the **integral gain** as well as the **proportional gain** refer to the settings of the feedback loop, the higher the faster it acts on the position of the tip. The **amplitude setpoint** is the amplitude of oscillation of the tip that the feedback loop tries to maintain constant by changing the tip position in the z axis direction. The unit of mV is converted into a value in nm that depends on the detector sensibility expressed in nm/V .

2.5 Measurement of the contact angle

An OCA20 goniometer from Dataphysics (Figure 2.4) equipped with an ultra fast CCD camera (1), was used to measure the water contact angle, the static roll-off angle and the dynamic roll-off angle for each coated fabric. These different measurements were performed with the software SCA20 and with Milli-Q water droplets of $10 \mu\text{L}$. We tried to minimize as much as possible the contact time (less than five seconds) between the droplet and the fabric surface before making the measurement. For these measurements, the sample is fixed as flat as possible on the sample holder (3) but without being stretched to avoid any deformation of the surface structure of the fabric. This allows a better estimation of the interface between the water and surface of the sample. The needle (2) dispenses the water droplet and the light source (4) provides contrast to the images filmed by the camera.

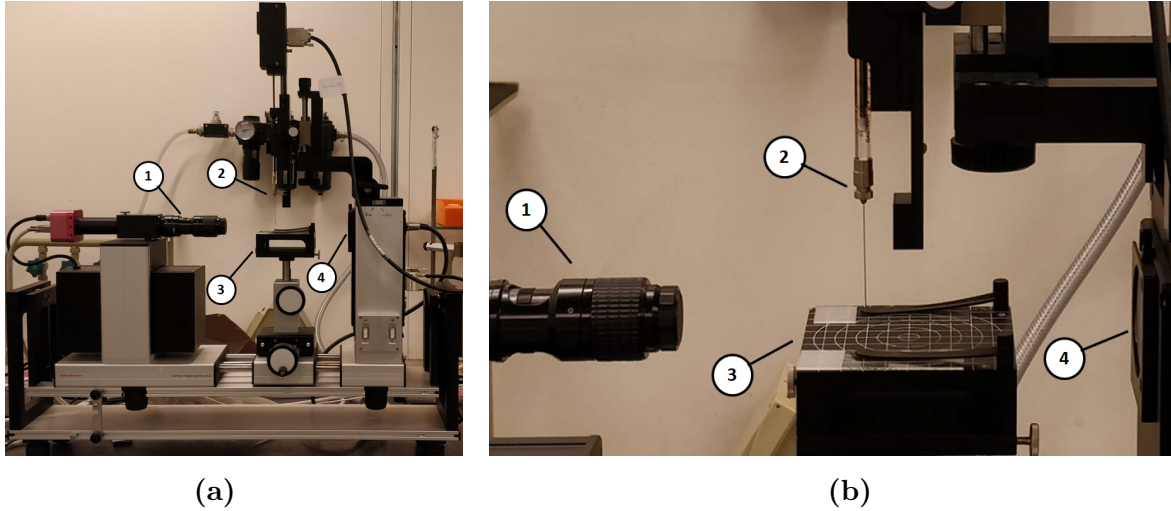


Figure 2.4 – General view of the goniometer used for the contact angle measurements. In both figures, the ultra fast CCD camera (1), the needle (2), the sample holder (3) and the light source (4) are indicated.

2.5.1 Measurement procedure for the three types of measurements

Contact angle measurement

Once the sample is fixed on the sample holder and is flat, a water droplet is slowly dropped off on the sample surface with the camera focused on it. The next step is then to indicate to the software the interface between the droplet and the fabric surface. That is why a flat sample surface is recommended. Afterwards, a direct estimation of the contact angle is possible by means of an *ellipse fitting* method included in the software. For each sample, this procedure is repeated at least four times, each being at different locations of the sample to ensure repeatability and estimate the standard error.

Static roll-off angle

As for the contact angle measurement, a water droplet is first dropped off on the flat sample surface. The entire instrument is then rotated until it reaches 90° . Figure 2.5 shows two different tilt angles for the instrument that were achieved by progressively increasing the angle of the instrument, as it was done for the static roll-off angle measurements. The droplet deposited on the surface is continuously filmed during the rotation of the instrument in order to detect the tilt angle of the device from which the droplet starts rolling-off from the surface. The tilt angle of the machine when the droplet rolls-off is called the static roll-off angle. One repeats this procedure several times at different places of the samples until one observes that there is no static roll-off angle or that a reasonable interval ($\leq 10^\circ$) for the static roll-off angle is obtained.

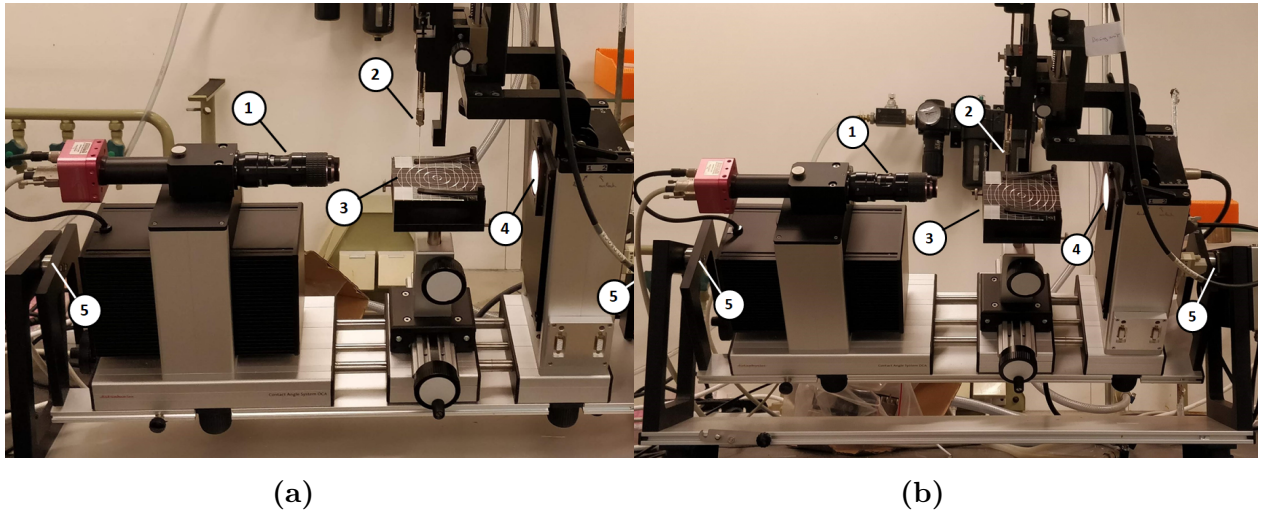


Figure 2.5 – General view of the goniometer used for the contact angle measurements at two different tilt angles times during its rotation. The static roll-off angles are measured by increasing progressively the tilt angle of the instrument. In both figures, the ultra fast CCD camera (1), the needle (2), the sample holder (3), the light source (4) and the axis of rotation (5) are indicated.

Dynamic roll-off angle

The instrument is first tilted to a certain angle (Figure 2.6) before carefully dropping off the water droplet onto the sample. It is important to do so to avoid dropping the water droplet from a certain height so that the water droplet does not have kinetic energy before reaching the fabric surface. Otherwise, the value of the measured dynamic roll-off angle would be slightly decreased.

The instrument is first tilted at a small angle. If the water droplet does not roll-off, the tilt angle of the device is further increased until the droplet rolls-off from the sample surface. This specific angle is called the dynamic roll-off angle. The trials were thus performed with an increasing tilt angle of the goniometer until the dynamic roll-off angle was reached. This sequence is repeated several times and at different places of the sample until a reasonable interval ($\leq 10^\circ$) for the dynamic roll-off angle is obtained.

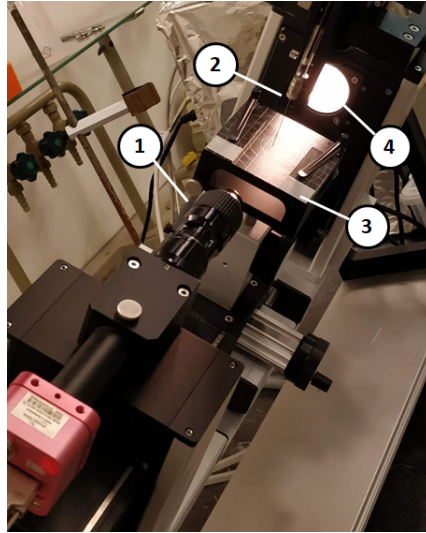


Figure 2.6 – View of the goniometer used for the contact angle measurements at a defined tilt angle. In both figures, the ultra fast CCD camera (1), the needle (2), the sample holder (3) and the light source (4) are indicated.

Chapter 3

Results and Discussion

This chapter is divided in three sections, each detailing and discussing the results obtained from each type of measurement. First, the measurements performed by stylus profilometry are presented and discussed. From these measurements, we intended to characterize the roughness of the surface at the macroscale by scanning large surface areas of the sample and computing a value for the roughness factor r defined by Wenzel (equation 1.1). Moreover, the problems we encountered and how the parameters were adjusted for this technique are explained.

In the next section, the results obtained from the Atomic Force Microscopy (AFM) measurements are described. As for the measurements performed with the stylus profilometer, we characterized the roughness of the sample, but this time, at the microscale. More precisely, the top of different fibers were scanned to identify the small scale features at their surface and evaluate if these features contribute to the fabric roughness. The roughness factor was thus computed from the data extracted by the AFM. This section ends with a discussion about the difficulties encountered with this technique and how the parameters were adjusted.

The third section presents and discusses the measured contact angles, static roll-off angles and dynamic roll-off angles for the coated samples. These measurements were done to evaluate the water-repellent properties of the fabrics. They allowed to estimate the water repellency of the coated fabrics and to compare the performances of each coating for a given fabric.

Finally, the combination of the measurements performed by stylus profilometry and AFM, together with the contact angles, static and dynamic roll-off angles, allowed us to assess the effect of surface texture on the wettability of the fabrics. In other words, the different types of measurements performed in this study allowed us to determine the influence of the fabric roughness on the water-repellent properties of the fabric in addition to the comparison between the performances of each coating.

3.1 Stylus profilometry measurements and estimation of the roughness of the fabrics

The stylus profilometer provides us a discrete 3D scan of the surface when following the procedure described in section 2.3. In order to compute the roughness factor r (equation 1.1), the original scan recorded via the stylus profilometer has to undergo a mathematical image treatment. This consists of two steps, flattening and deglitching (if needed) and it is detailed further in this section. Before that, the results obtained from the data acquired with the stylus profilometer are presented and discussed. Deeper explanations are also given on how we managed to obtain high quality scans for rougher samples by stylus profilometry. Thereafter, the specific case of the Fabric7 sample is discussed as well as how we determined the optimal scanning parameters for the protocol of measurement with this instrument. Finally, we analyze the systematic errors of the stylus profilometer before drawing the main conclusions from this first section.

3.1.1 Results

Table 3.1 provides the computed roughness factors (equation 1.1) for each analyzed sample. As a reminder, for each fabric we had four samples: three with the respective coatings used in this study, and one is the original fabric. Section 1.3 introduced the two different weaving patterns on each side of the Fabric7 sample. For the twill weave side (face A), two different values for the roughness factor were obtained depending on the scanning direction. This is discussed in section 3.1.4. The seven fabrics at our disposal for this study cover a wide range of roughness from $r = 1.19$ to $r = 1.86$. This large range is interesting to assess the effect of fabric texture on the water repellent properties of the coated polyester fabrics .

Sample name	Uncoated	PDMS	PM900	SchPFF
Fabric1	1.19	1.19	1.16	1.21
Fabric2	1.27	1.27	1.24	1.28
Fabric3	1.45	1.52	1.54	1.46
Fabric4	1.51	1.52	1.56	1.56
Fabric7 face A	1.61/1.86	1.56/1.84	1.56/1.73	1.56/1.71
Fabric7 face B	1.68	1.68	1.59	1.60
Fabric5	1.64	1.70	1.66	1.59
Fabric6	1.78	1.86	1.85	1.73

Table 3.1 – *Roughness factors of the different fabrics obtained by the stylus profilometry measurements.*

The first observation one can make from Table 3.1, is that the coatings did not significantly change the apparent surface roughness of the original fabric. For a given type of coating, the apparent macroscale roughness increases or decreases slightly for the different fabrics. The variation of the roughness factor for one given fabric, does not exceed 10% compared to the smallest computed value (valid for all fabrics). Additionally, the comparison of the different fabrics shows that a given coating sometimes leads to an increase or a decrease of r . The explanation for these variations of r probably resides in the intrinsic properties of the fabrics. When meters of fabrics are woven on industrial scale, one cannot ensure that the textile shows exactly the same properties for each square millimeter of the surface. Considering this, it seems fair to say that the three different types of coating are not responsible for the change of the sample roughness at the macroscale. Moreover, it was observed that the three coatings are almost transparent and do not damper the color of the fabrics.

3.1.2 Solution to imaging problems with the profilometer

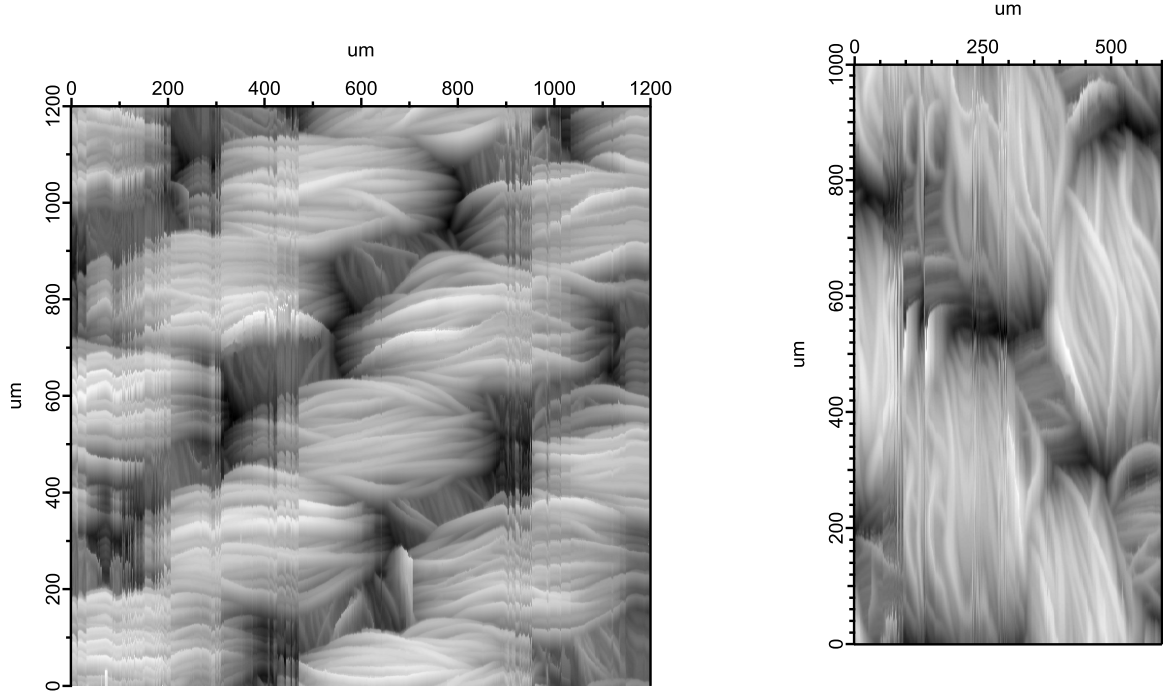
Naturally, the images used to obtain the roughness factor need to be as accurate as possible. To do so, one needs mainly to avoid glitches and misalignment between the parallel line profiles that are used to build up the 3D image of the surface. At first, when starting this study, it was very difficult to obtain images without important misalignment of the line profiles or glitches, especially for rougher fabrics. The first step of this study was thus to optimize the protocol of measurement to obtain better images with the stylus profilometer.

We started our research of the optimal scanning parameters with the Fabric7 sample (face A). At that time, there was no knowledge that this sample had two different sides. This sample was chosen based on first estimations from previous images (of lower quality). The Fabric7 sample presented a roughness ($r \simeq 1.7$) slightly lower than the roughest samples (Fabric5 and Fabric6 with $r \simeq 1.75$ and $r \simeq 1.86$, respectively). It was hoped that finding optimal scanning parameters for a sample of intermediate roughness would be easier and would allow us to use these same optimal parameters for the other samples.

Following this line of reasoning, several scans of the Fabric7 sample were performed varying the scan speed, the resolution, the stylus force and the range. Yet, the same important problems of misalignment of the line profiles persisted for different combinations of parameters and no optimal parameters were found at that time.

However, after performing a couple of scans with changing parameters, we noticed they had all one thing in common: the misalignment of the line profiles was particularly important when the tip started line profiles at points measured below the zero height level (h_0) defined by the instrument. In contrast, several consecutive line profiles with starting points well above h_0 presented a good alignment. In Figure 3.1, one can clearly see the

regions where the line profiles are not well aligned, causing low quality images that are not suitable for the calculation of the roughness factor.



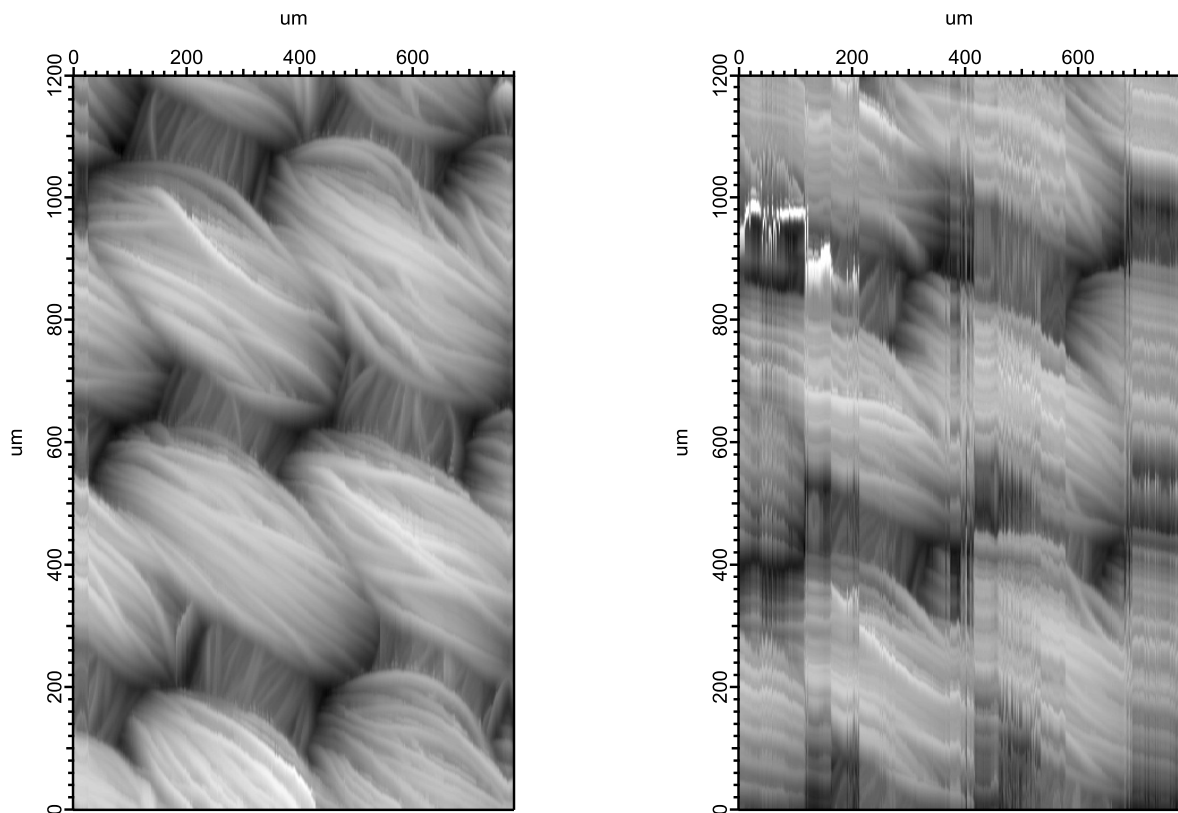
(a) Wide scan of the Fabric7 sample where misalignment occurs for starting points in darker areas, i.e., for points below the defined zero height level h_0 . Greyscale ranges from 0 to 182 μm .

(b) Scan of the Fabric7 sample where misalignment occurs for starting points in darker areas, i.e., for points below the defined zero height level h_0 . Greyscale ranges from 0 to 163 μm .

Figure 3.1 – Both images are part of the first scans done to find optimal parameters to image the fabrics with the stylus profilometer. These two scans have an orientation difference of 90° but show the same problems, when the tip starts (bottom of the images) at points below the defined zero height level h_0 (darker regions), misalignment of the parallel line profiles occurs.

To verify this observation, one had to find a way to make the tip start at points above h_0 for the entire width of the scan. Luckily, we started working on the Fabric7 sample with the face presenting the twill weave (face A). As explained in section 1.3, for a twill weave, weft yarns stick out on a diagonal (Figure 1.5c). Furthermore, the starting points of the different line scans are on the x axis and the scanning direction is parallel to the y axis. If we achieved to orient and position the sample such that the diagonal of the sticking out weft yarns is placed on the x axis, each line profile would then start on the diagonal, at points above the zero height level defined by the stylus profilometer. We explored that possibility and it appeared to be conclusive. After a few attempts to place the x axis perfectly on the maxima of the diagonal, we achieved to obtain good images and the result is shown in Figure 3.2a.

To confirm that the misalignment problem was due to line profiles with starting points positioned below h_0 , we performed a scan with the exact same parameters as for the image in Figure 3.2a, except that we positioned the x axis in between two diagonals of sticking out weft yarns. All the points of the x axis were thus below h_0 and the result of this scan is illustrated in Figure 3.2b. This scan confirmed our thoughts. Yet, the placement of the x axis needed to be really precise in order to obtain a good image is in Figure 3.2a. Therefore, the right placement of the x on the diagonal sticking out of the surface might need several tries before the finding the right position.



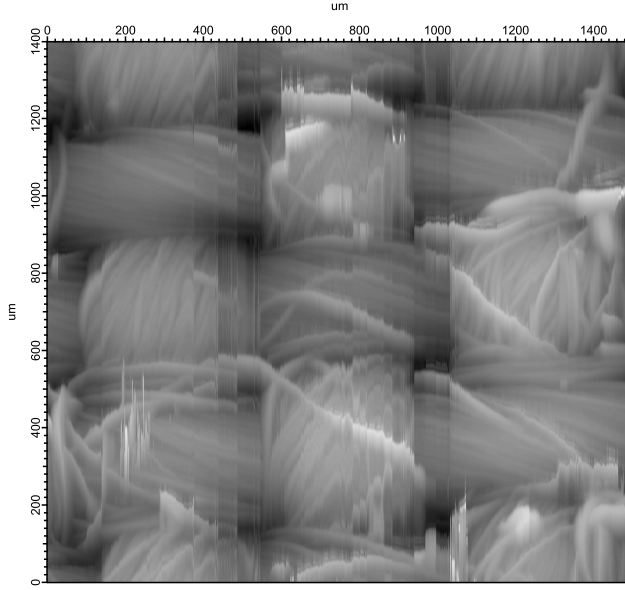
(a) Scan of the Fabric7 sample when the x axis is positioned on the top of the diagonal of the sticking out weft yarns. Greyscale ranges from 0 to 179 μm .

(b) Scan of the Fabric7 sample when the x axis is positioned in the valley between two diagonals of sticking out weft yarns. Greyscale ranges from 0 to 246 μm (glitch).

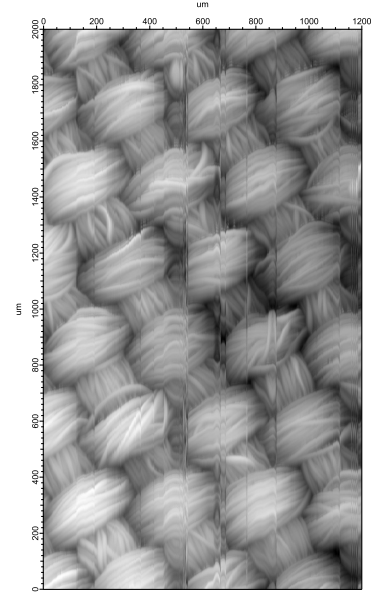
Figure 3.2 – These two scans verified our hypothesis that misalignment occurred when line profiles start at heights below h_0 . The difference between the two images only resides in the position of the x axis (where the line profiles start). All the other scanning parameters are the same.

The next step was thus trying to apply this protocol to the other samples. Unfortunately, it did not work out for the rougher fabrics as one can see in Figure 3.3. From Table 2.1, we know the Fabric7 sample (face A) is the only one to show a twill weave pattern. The other fabrics present a plain weave and show a basic cross pattern

(Figure 1.5b). Therefore, regardless of the scanning direction and orientation of the sample, there is always a minimum below h_0 on the x axis between a weft and/or a warp yarn causing misalignment. It was then obvious we would not achieve to have all starting points of the line profiles at heights above h_0 only by precisely configuring the orientation of the sample. Therefore, we had to find another way to perform properly the measurements for all fabrics including the Fabric7 sample (face A).



(a) Scan of the Fabric5 sample for which we tried to have the x axis above h_0 . Greyscale ranges from 0 to $385 \mu\text{m}$.

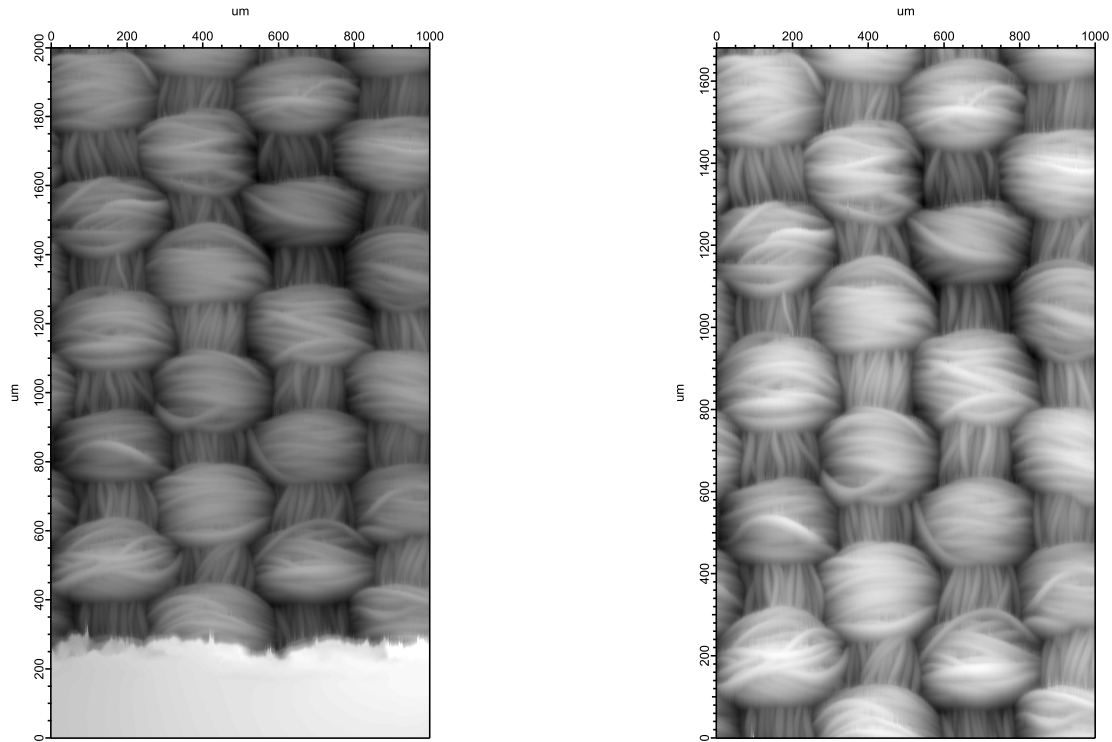


(b) Scan of the Fabric3 sample for which we tried to have the x axis above h_0 with a specific orientation. Greyscale ranges from 0 to $143 \mu\text{m}$.

Figure 3.3 – These two images show the Fabric5 and Fabric3 samples. Although it was tried to position the x axis above h_0 , it was not possible to perform a proper measurement along the entire axis because of the misalignment of line profiles.

We thus came up with the idea of sticking a thin and smooth height reference tape onto the surface of the fabric. This allowed us to have a constant starting height for each line profile, above the sample surface. Additionally, the tip approach was made easier because of the smooth tape surface. Therefore, the accuracy of the starting point was also increased. Though it is not well understood how h_0 is defined by the stylus profilometer, having the tape placed on the sample allowed us to have the x axis above h_0 . This simple and very cheap solution turned out to be very effective and high quality images could be achieved for all the fabrics regardless of their roughness and weave pattern as can be seen in Figures 3.4 and 3.6 for instance.

The roughness factors for the different samples were calculated from scans recorded on samples with tape stuck on their surface. The images then just needed to be reframed to remove the part of the image where the tape is scanned as illustrated in Figure 3.4. This figure shows a scan of the Fabric3 sample before and after reframing.



(a) Original scan of the Fabric3 sample with the tape at the bottom of the image. Greyscale ranges from 0 to 242 μm .

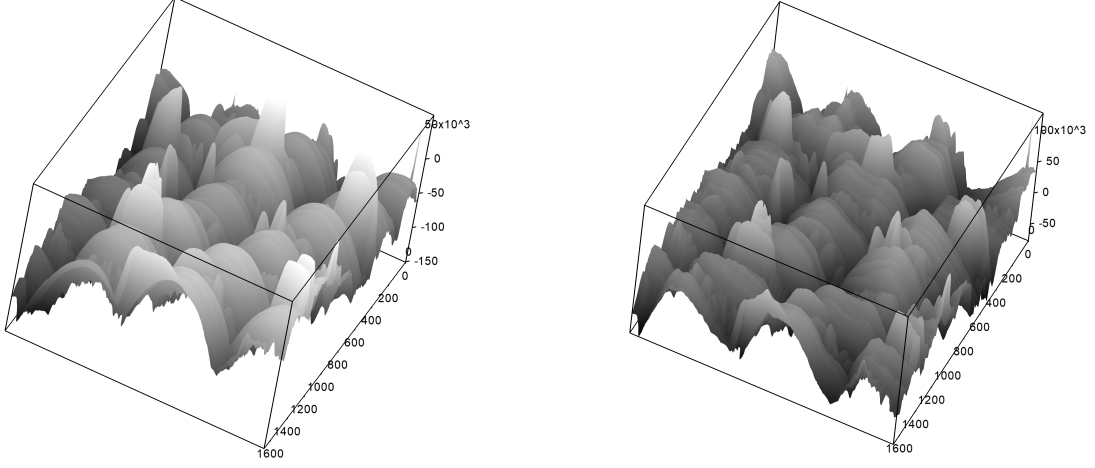
(b) The original scan of the Fabric3 sample reframed to remove the part with the tape. Greyscale ranges from 0 to 151 μm .

Figure 3.4 – The Fabric3 sample that was scanned using the solution of the tape stucked onto the fabric surface.

3.1.3 Image treatment

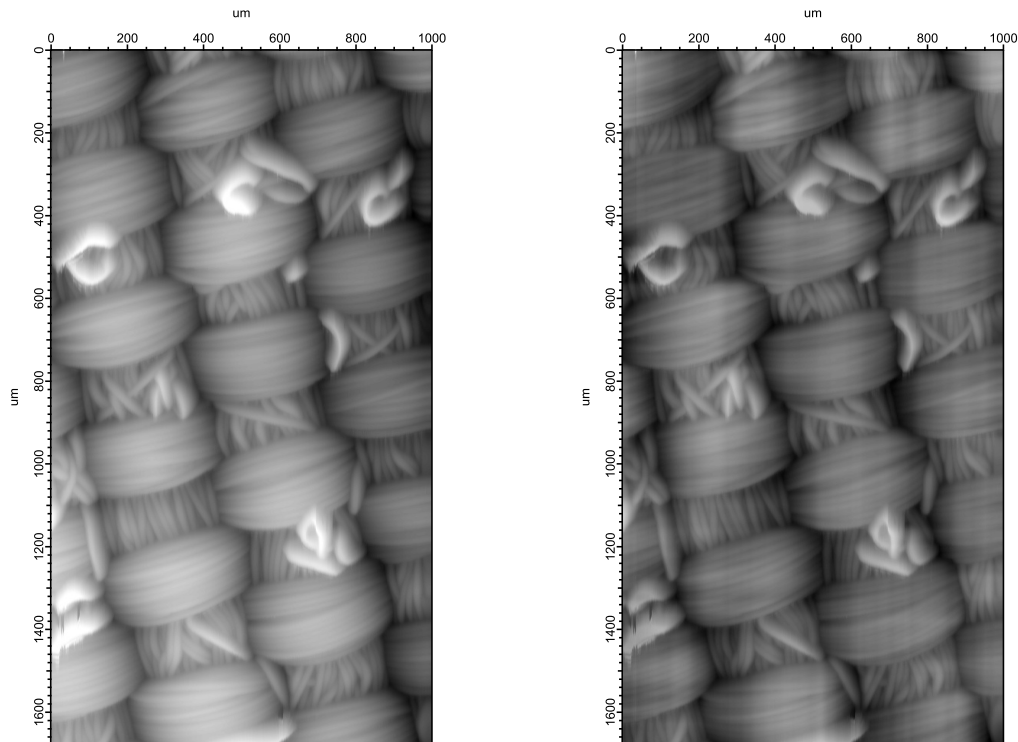
The scans we obtained after the placement of the tape onto the fabric surface, were of high quality but still needed to be adjusted before computing the roughness factor r of the surface. In addition to reframe the scan, one may need to flatten the image and deglitch it. The flattening treatment that occurs before the calculation of r is illustrated in Figures 3.5 and 3.6. An image obtained directly from the stylus profilometer is presented in Figure 3.5a and one can clearly notice the inclination of the sample between the left front corner and the right back corner. Figure 3.5a is the 3D perspective computed from Figure 3.6a and the inclination is visible as well. This original scan image needs thus to be flattened before computing r . Figures 3.6b and 3.5b show the images obtained from Figure 3.6a and 3.5a, respectively, after flattening by using image analysis routines (see appendix D.1 for the code of the routine) developed in IgorPro by Profs. A. Jonas and B. Nysten. The performed flattening is done on a case-by-case basis though for most of them, a linear

flattening over the whole image allowed us to achieve the expected result. The example shown in Figures 3.6 and 3.5 is a scan of the Fabric4 sample without any coating. The flattened images used to compute r for all the others samples can be found in appendix A.



(a) *Fabric4 sample before image flattening.* (b) *Fabric4 sample after image flattening.*
 Greyscale ranges from 0 to 216 μm . Greyscale ranges from 0 to 206 μm .

Figure 3.5 – Comparison of the three-dimensional images between the original image obtained from the stylus profilometer and the flattened image.



(a) *Fabric4 sample before image flattening. Greyscale ranges from 0 to 216 μm*

(b) *Fabric4 sample after image flattening. Greyscale ranges from 0 to 206 μm*

Figure 3.6 – Comparison between the original image obtained from the stylus profilometer and the flattened image.

The second encountered artifact lowering the quality of the scans performed with the stylus profilometer are glitches, in particular for rougher samples (mainly Fabric5 and Fabric6 in our study). Glitches are due to loose fibers that stick on the tip. In that case, the stylus has to move up more than it would normally do to lose contact with that loose fiber. As a result, during the time needed for the tip to get rid of the fiber, the next sampling points are extremely high compared to the rest of the surface and a glitch is caused in the resulting image. During that same time, the tip is not in contact with the surface anymore causing these points to be irrelevant. The sampling points of very high heights have to be treated so that the roughness factor is not overestimated.

This was done by two means. First, choosing 'valleys' for the stylus profilometer 'mode' parameter (see Table 2.4). By doing so, points of heights below h_0 are accurately measured whereas a maximum height value is assigned to points showing heights above h_0 . The use of this mode makes sense since the tape is applied on the fabric surface. Hence the points of interest are the ones with heights that are below the height measured for the tape.

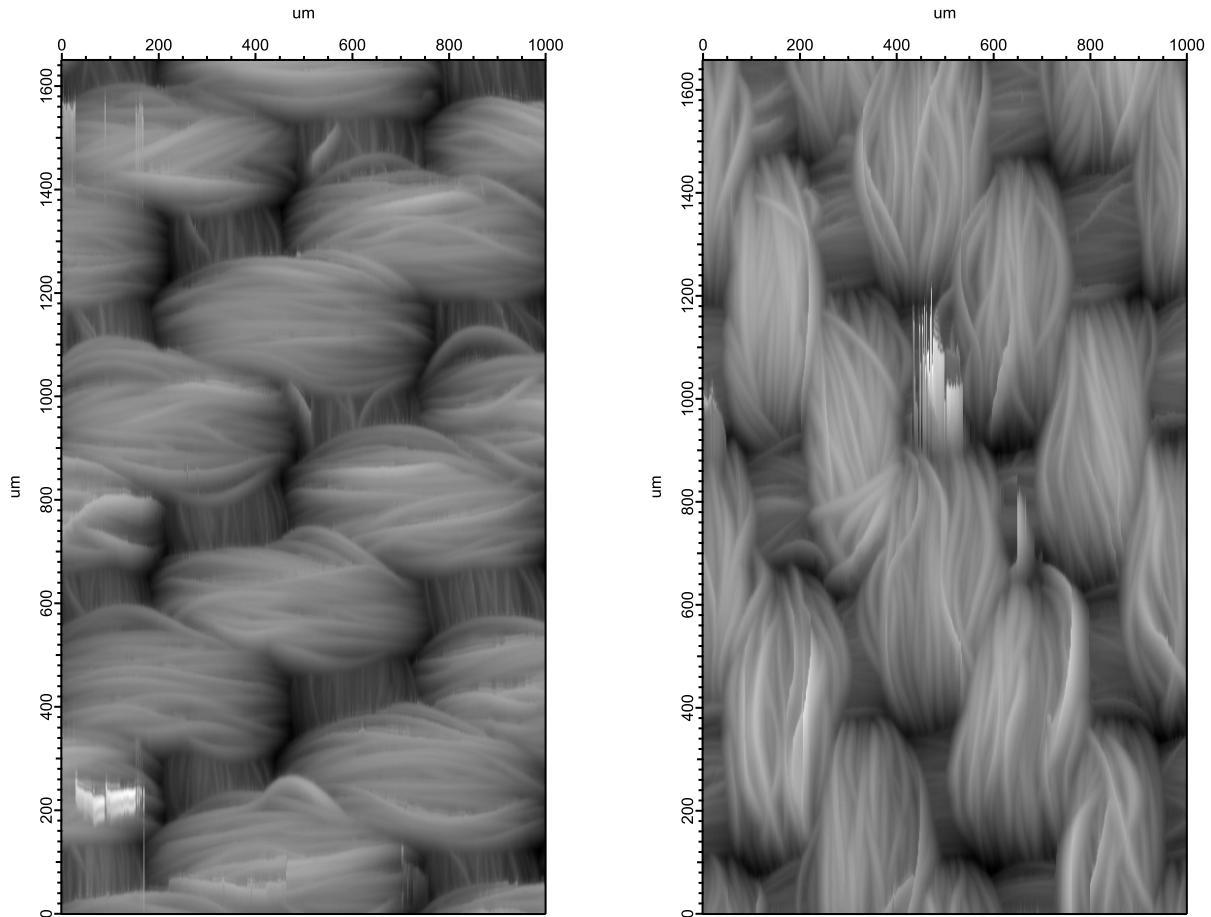
Second, image treatment also reduces the impact of glitches on r measurements. By means of the homemade routines with IgorPro, one can limit the maximum and minimum

value of the derivatives in equation 1.10 when calculating the actual surface area for each pixel. For glitches, the values of the derivatives in this equation are much higher and thus an overestimated surface area would be calculated. Imposing limits to the derivatives thus reduces the effect that glitches can have on the computed value of r .

Unfortunately, we have not found any solution to prevent fibers from sticking to the stylus tip, thus creating glitches, without impairing the surface. Yet, the mathematical image treatment is efficient and allows to deal with glitches when they are in small number. Moreover, the presence of glitches can not really be anticipated and varies from one area of the sample to another. Performing a very wide scan (which is time consuming) can be interesting to identify surface areas of the sample containing few or no loose fibers that could create glitches.

3.1.4 Difficulties with the Fabric7 sample

The Fabric7 sample appeared to have two different sides. The two sides exhibit a different weave pattern as explained and illustrated in section 1.3. Therefore, we considered each side like two different samples. The side named 'face B' exhibits a weave closer to a plain weave than a twill weave. No specific problems were encountered for the scanning of this side of the fabric and with the computation of the roughness factor. However, for the twill weave side, i.e. 'face A', the roughness factor was significantly different, depending on the orientation of the sample versus the scanning direction. As one can see in Figures 3.7a and 3.7b, the details of the yarns sticking out are better resolved in Figure 3.7b. Because the tip travels from the bottom to the top of the image, height drops are much more sudden in Figure 3.7a when the tip travels perpendicularly to the sticking out yarns, than in Figure 3.7b, where the tip runs along these yarns, and undergoes smaller and smoother height variations in that case. This causes the image displayed in Figure 3.7b to be sharper compared to the perpendicular scanning direction illustrated in Figure 3.7a. In addition to the difference of resolution of the fibers in the obtained images, the value obtained for the roughness factor is also different. From Figure 3.7a, the obtained roughness factor is equal to 1.61 (glitch treatment included) while for Figure 3.7b the obtained roughness factor is equal to 1.86 (glitch treatment included).



(a) Face A of the Fabric7 sample scanned perpendicularly to the weft yarns sticking out. Greyscale ranges from 0 to 242 μm (glitch).

(b) Face A of the Fabric7 sample scanned parallel to the weft yarns sticking out. Greyscale ranges from 0 to 253 μm (glitch).

Figure 3.7 – Comparison of the images obtained for the Fabric7 sample (face A) when varying the orientation of the sample of 90° .

However, the roughness factor for a scanned surface area can only have one possible value. Though it would seem logical to say that the roughness factor obtained from Figure 3.7b is more accurate because the yarns are better resolved, we decided to investigate further. To do so, we first scanned the sample with an orientation exactly in between the two previous orientations, with the x axis parallel to the diagonal of weft yarns sticking out of the surface (Figure 3.9). The roughness factor resulting from this scan was equal to 1.73 (exactly in between the ones obtained for the two other orientations). Secondly, we scanned the sample in the same orientation as in Figure 3.7a but at much lower scan speed. More precisely, the scan speed was reduced by a factor ten. Seventy seconds were necessary for the tip to travel the defined scan length of two millimeters (more than ten hours were necessary for such a scan). Therefore, the number of data points per line profile also increased by a factor ten. This low scan speed provided much more time to the tip to adapt to sudden height drops which resulted in a sharper resolution of the yarns as shown in Figure 3.8. From this scan, the resulting roughness factor is equal to 2.05. This result

is much higher than for all the other samples. It is thus probable that the roughness we measure is relative to a given scanning rate. Therefore, we decided the roughness factor of this sample to be the average between the ones obtained from the two different scanning directions presented in Figure 3.7 which were obtained with the same scan rate as for the other images. It is however important to be aware that the roughness factors we computed are relative numbers. This is thus sufficient to compare different samples, but might be a problem for more quantitative analyses.

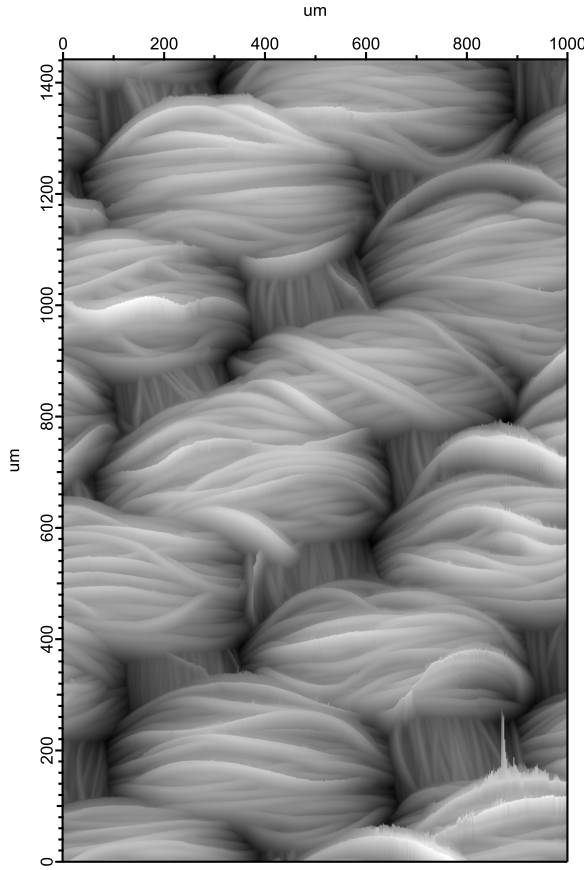


Figure 3.8 – Face A of the Fabric7 sample scanned perpendicularly to the sticking out weft yarns measured at very slow scan speed. Greyscale ranges from 0 to 204 μm .

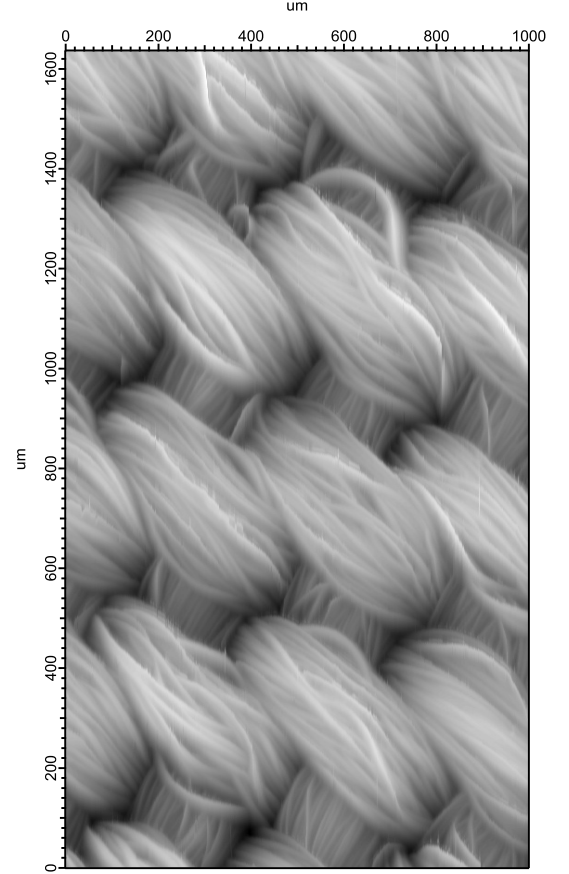


Figure 3.9 – Face A of the Fabric7 sample scanned at 45° compared to the sticking out weft yarns. Greyscale ranges from 0 to 189 μm .

3.1.5 Adjustment of the measurement parameters

Table 2.4 provided the parameters used for the stylus profilometer when scanning the samples with the tape stucked on it. The reasons for the choice of these parameters are explained below.

The **range** can be set to four different values which are 6.5 μm , 65.5 μm , 524 μm and 1 mm. These values describe the maximum range that the stylus can have in its vertical movements (z axis). The used range has to be higher than the height difference between

the minimum and maximum recorded heights so that the stylus can precisely scan the defined area. On the other hand, it has to be as close as possible to this same height difference to have a maximum sensitivity for small height variations. Since for the smoother samples this height difference between the maximum and minimum height is of the order on *ca.* 150 μm and that the one of the rougher samples is of *ca.* 250 μm , the best possible choice for the range parameter is 524 μm .

The choice of **mode** can be 'hills', 'valleys' or 'hills and valleys'. The mode 'hills' only records heights above the defined zero height level h_0 whereas the mode 'valleys' records only heights below that same zero height level (defined by the stylus profilometer). The mode 'hills and valleys' combines both and records heights below and above the zero height level. The choice of the mode 'valleys' has been explained in section 3.1.3 and is interesting to limit the effect of glitches on the computed roughness factor.

The **stylus force** has been set to 1 mg because this force showed good results. We tried higher values for the stylus force but the resulting images were not as good in terms of quality. This parameter was thus determined based on a trial and error approach.

The geometrical dimensions of the scanned surface area, i.e. the **map extend** (x axis) and **length** (of the line profile, y axis), were arbitrarily chosen so that the image used for the computation of the roughness factor (after the original scan has been reframed) includes several repeating unit cells in order to provide an average r . By doing so, we expect to obtain a more representative value for the roughness factor of the fabric. Increasing the scanned surface area also increases the scanning time which is already of *ca.* two hours with the chosen parameters. A good balance has thus to be found between the scanning time and the scan size used to estimate r .

The smaller the **stylus radius** of the tip, the better the resolution of the final scan as explained in section 1.1.2. The smallest tip at our disposal had a radius of 0.7 μm and therefore, this parameter could not be changed.

The **map resolution** parameter describes the distance between the parallel line profiles, in other words, it determines the lateral resolution. A lateral resolution of 2 μm was thought to be a good compromise between the scanning time and the resolution obtained. Since the diameter of the fibers of the different fabrics is *ca.* 10 μm , it seems to be an appropriate lateral resolution to clearly distinguish the fibers of the fabric. One needs to be aware that reducing the map resolution to 1 μm (which is the lowest the DektakXT from Bruker can achieve) is more than double the scanning time, since the amount of parallel line profiles performed by the stylus profilometer is doubled. As for the geometrical dimensions of the scanned area, one has thus to weigh up the pros and cons in order to determine a good compromise.

The choice of the map resolution automatically determines the number of **traces** (line

profiles) carried out by the stylus profilometer. Since the map extend and map resolution have been set, the amount of traces is the ratio between the map extend and the map resolution.

The **duration** has been set to seven seconds to obtain a resolution of *ca.* $1\ \mu\text{m}$ in the scanning direction. First, it allows to have a reasonable scanning time, and second, it is near the maximum resolution the tip can achieve since it is limited by its diameter. Actually, going slower gives more time to the tip to adapt to sudden height variations. Hence, it increases the height measurement accuracy but it does not reduce the limiting size of the grooves the tip can detect.

The duration, together with the scan length parameter, determines the values for the **resolution**, **points** and **speed** parameters. These three parameters are automatically calculated in function of the values set for the duration and the scan length. However, one has to keep in mind that the duration was chosen in order to achieve a certain resolution and not the opposite.

3.1.6 Measurement reliability and assessment of the random errors of the stylus profilometer

To assess the reliability of the measurements done with the stylus profilometer for the different samples, we arbitrarily chose one sample to evaluate the influence of the random errors of the instrument on the computed roughness factor. To do so, the same surface area of the Fabric3 sample was scanned five times in a row. For each scan, the roughness factor was calculated following the same procedure as for the other samples. First, reframing the image, then flattening it (if needed) and deglitching it (if needed) to finally calculate r . A second area of the same sample was scanned two times to see if the trend obtained from the five previous scans was the same. The results of this repeatability test are presented in Table 3.2. They clearly show that the values are repeatable and that the random errors of the stylus profilometer are not important enough to affect the computed values of r . Therefore, for the other samples, only one scan was performed.

Scan 1.1	$r = 1.47$
Scan 1.2	$r = 1.47$
Scan 1.3	$r = 1.47$
Scan 1.4	$r = 1.47$
Scan 1.5	$r = 1.47$
Scan 2.1	$r = 1.46$
Scan 2.2	$r = 1.46$

Table 3.2 – *Computed values for the roughness factor of Fabric3 sample. Five scans were performed (from 1.1 to 1.5) on a first surface area. For a second surface area of the same sample, two scans were performed (2.1 and 2.2).*

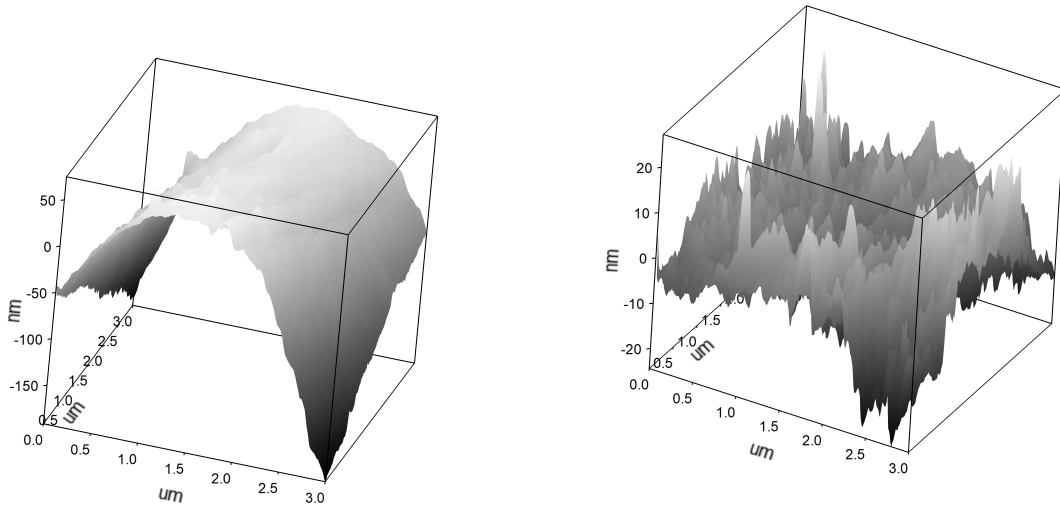
3.1.7 Conclusion from these results

The different results presented show that stylus profilometry is a useful and reliable technique to estimate the roughness of materials. However, applying it to fabrics appeared to be difficult because of the important height variations along the x axis on their surface causing misalignment of the parallel line profiles and glitches that can degrade the quality of the scans. Fortunately, a solution was found to avoid misalignment of the parallel line profiles, which was the major problem. It simply consists of sticking a piece of thin and smooth tape on the surface of the fabric. The resulting scans were of higher quality than the ones achieved without this trick. Concerning potential glitches, we have not found a way to avoid them without altering the samples. Nevertheless, a wide scan can be performed to detect surface areas less subject to glitches. The scans performed with tape were first reframed, then flattened and deglitched (if needed) before calculating the roughness factor. The different samples cover a wide range of roughness and the coatings did not cause any specific variation of roughness. The small differences between the different samples of a given fabric are essentially due to the variation of the fabric structure properties. Finally, the random errors of the stylus profilometer are much smaller than the difference of roughness between the different samples.

3.2 AFM measurements and estimation of fiber roughness

Scanning the different samples with AFM allowed us to compute the roughness factor at the surface of a single fiber of the fabric. This is only possible because of the very high sensitivity of the AFM to micro and nanoscale features.

As mentioned in section 2.4.2, two scan sizes of images were performed, $8 \times 8 \mu\text{m}^2$ and $3 \times 3 \mu\text{m}^2$. Since the fiber diameter is on the order of $10 \mu\text{m}$, the larger size image allows to center and identify the fiber properly. The smaller scan sizes allow to zoom on the centers of the larger images. Scanning the samples is for most fabrics easier with the small scan size. For the larger size images, being close to the dimensions of the fibers makes it harder to position the tip correctly in order to image only one fiber. The adjustment of the parameters was therefore more complicated for the $8 \times 8 \mu\text{m}^2$ images. For the calculations of r , we only used the $3 \times 3 \mu\text{m}^2$ scans but kept the scan of $8 \times 8 \mu\text{m}^2$ as additional data if needed. As for the scans obtained from the stylus profilometer, the original images need to be flattened before the roughness factor can be calculated. The curve due to the cylindrical shape of the fibers needs to be removed as illustrated in Figure 3.10. One of the four scans performed for each sample is presented in appendix B.2 (flattened images).



(a) Three-dimensional image computed from the original scan obtained from the AFM. Greyscale ranges from 0 to 266 nm.
 (b) Three-dimensional image of the same scan once the surface has been flattened through image treatment. Greyscale ranges from 0 to 52 nm.

Figure 3.10 – The two figures represent the same surface except that one is the original scan directly obtained from the AFM whereas the right one is the same surface once it has been flattened (Fabric4 sample without any coating).

3.2.1 Results

The average roughness factors computed for the scans of the fibers of each fabric are presented in Table 3.3 for the four types of samples per fabric. This average is based on two or three scans of the sample from the four available (detailed results in appendix B.1). All four scans of one sample were not used because the image flattening turned out to be complicated for some of them. Typically, scans where the fibers are not parallel to the y direction, are difficult to flatten. Moreover, the image treatment is generally time consuming and the roughness factors computed were identical or only slightly different from one scan to the other. A much different value for the roughness factor than the ones in Table 3.3 would have been surprising regarding the consistency of the obtained results.

Sample name	Uncoated	PDMS	PM900	SchPFF
Fabric1	1.00	1.00	1.01	1.01
Fabric2	1.01	1.00	1.00	1.00
Fabric3	1.00	1.00	1.00	1.00
Fabric4	1.01	1.00	1.00	1.01
Fabric5	1.01	1.01	1.00	1.00
Fabric6	1.01	1.01	1.08	1.10
Fabric7	1.01	1.00	1.00	1.00

Table 3.3 – *Average roughness factors obtained from the AFM scans performed on fibers.*

This table makes quite clear that the small imperfections that are found at the surface of the fibers are not significant and do not bring a considerable contribution to the roughness of the fabrics. The only exceptions are for the roughness factors computed for the Fabric6 sample coated with PM900 and SchPFF. Yet, the roughness factor for the uncoated fabric Fabric6 is of 1.01 as for the one coated with PDMS. In other words, if the measurements are fully accurate, it would mean that the coatings PM900 and SchPFF bring a microscale roughness to this sample. Considering the results for all the other fabrics and the results from the silicon wafers (Table 3.5), we can exclude this hypothesis. Indeed, scanning the silicon wafers with AFM revealed that these samples had a roughness factor $r = 1$ (i.e. completely flat surface) after the different coatings were deposited onto their surface. It is therefore likely that the values obtained for the Fabric6 sample are affected by larger errors.

3.2.2 Difficulties with the Fabric6 sample

With the stylus profilometer, the Fabric6 sample showed the highest macroscale roughness. This is notably due to the higher amount of loose fibers and the important irregularities of the surface because the yarns are less stretched than for smoother samples. Altogether, this also causes the Fabric6 sample to be particularly hard to scan by AFM.

The first challenge with Fabric6 sample is to approach the tip on the sample surface. Because of loose fibers sticking out, or just adjacent yarns being higher than the one to be scanned, the electronic device sometimes refuses to approach the tip to the surface because the instrument considers there is a risk of crashing the tip.

Secondly, if one succeeds to approach the surface and that the tip is in (intermittent) contact with the surface, positioning the tip in order to image only one fiber also appeared to be difficult. There again, the important (at the scale of the size image) height variations of the sample makes the positioning of the tip difficult. By moving the position of the tip, the cantilever may be blocked by other fibers. As a result, the signal spins out of control and one has to find a better area to scan. It was frequent to test several areas before achieving a good scan.

Finally, when the fiber is clearly identified and that the scanning of the fiber occurs without any problems, the 'trace' and 'retrace' signals have to be as identical as possible to have a good measurement. Once more, it appeared to be difficult to have the 'trace' and 'retrace' signals properly superimposed for this fabric. Even increasing the reaction rate of the feedback loop at its maximum (before having noise in the signal) did not provide a very high similarity between both signals. The lower tension in the yarns of this rougher fabric causes the fibers to move slightly during the scan. Therefore, the 'trace' and 'retrace' signals do not exactly superimpose.

All things considered, the Fabric6 sample was much harder to image properly with the AFM compared to the other samples, due to the reasons discussed above. The experimental error is therefore probably higher for this sample though we tried to record the best possible scans. Hence, we think the higher values obtained for r with the Fabric6 sample coated with PM900 and SchPFF are most likely due to less accurate scans. In fact, the differences in the roughness factors calculated for this sample are much more important than the ones for all the others. Table 3.4 regroups the roughness factors computed from the different scans performed on the Fabric6 sample for each coating. As one can see, the two first samples (uncoated and PDMS) have similar roughness factors while for the coatings PM900 and SchPFF, the values calculated for r differ a lot from one to another. Therefore, we concluded that the samples Fabric6 coated by PM900 and SchPFF had a similar fiber roughness than the fabric without any coating and that the obtained results were mainly due to the difficulty to perform good measurements on these samples.

	Uncoated	PDMS	PM900	SchPFF
Fabric6	1.00	1.01	1.06	1.04
	1.01	1.01	1.13	1.16
	1.01		1.06	
Average r	1.01	1.01	1.08	1.10

Table 3.4 – *Roughness factors computed for the scans performed with AFM for the Fabric6 sample and the resulting average roughness factor.*

3.2.3 Roughness of coatings deposited on silicon wafers

In Young-Dupré model (see equation 1.12), the measured contact angle (θ_Y) is the one measured on a completely flat and chemically homogeneous surface. Since all the other models try to explain the observed contact angle on the basis of this specific contact angle, it is important to evaluate it. In order to respect the conditions described in Young-Dupré model, we used a silicon (Si) wafer as a flat reference surface and covered it with the respective coatings used in this study (see section 2.2.3). To verify that the coated silicon wafers are flat as assumed, we scanned them by AFM. The same $3 \times 3 \mu\text{m}^2$ scan size was used with a scan rate of 1 Hz. The computed roughness factors for each scan are presented in Table 3.5. From these scans performed with the AFM on the silicon wafers, we concluded they could be considered as flat surfaces and that the coatings did not provide any microscale roughness to the fabrics. Consequently, the contact angle measured on these samples can be considered as the contact angle defined in Young-Dupré law.

	PDMS	PM900	SchPFF
Si wafer	1.00	1.00	1.00
	1.00	1.00	1.00
	1.00	1.00	1.00
Average r	1.00	1.00	1.00

Table 3.5 – *Roughness factors obtained for three different scans of $3 \times 3 \mu\text{m}^2$ for each type of coating deposited onto the silicon wafers.*

3.2.4 Adjustment of the parameters

Table 2.5 describes the parameters used for the AFM measurements. The reasons for the choice of these parameters are explained below.

The **scan size** was arbitrarily chosen as explained previously. However, the choice was not random. Since the goal was to estimate the roughness of the fibers, we had to record images smaller than the diameter of the cylindrical shaped fibers to be certain to scan only one fiber at a time. We knew the fiber diameter to be on the order of *ca.* $10 \mu\text{m}$, so the first scan size of $8 \times 8 \mu\text{m}^2$ allowed us to locate a fiber while the second scan size of $3 \times 3 \mu\text{m}^2$ allowed us to zoom in on the fiber and evaluate more precisely the microscale roughness at the fiber surface.

The **scan rate** was set to 0.75 Hz at the beginning before using 1 Hz. The scan rate, among other parameters, determines the acquisition time for one image. At first, using 0.75 Hz seemed to be a good compromise to have good images. Yet, increasing the scan rate to 1 Hz did not reduce the accuracy of the scan but the configuration of the feedback loop reaction speed was more sensitive. Since the time needed to acquire one scan with a scan rate of 1 Hz is lower and did not cause the image to be of a lower quality, we

continued that way. One may add that the difference between 0.75 Hz and 1 Hz for the scan is not substantial, and therefore, the sensitivity of the feedback loop was only slightly increased.

The parameters **sampling points/line** and **number of lines** defined the resolution of the image. By setting these two parameters to 256, the final image has 256×256 pixels. This resolution is considered to be sufficient for the calculation of the roughness factor.

The **integral** and **proportional gains** are two parameters corresponding to the tuning of the feedback loop and thus of its reaction speed.

The proportional gain tuning did not truly affect the topographical signal because the effect it has on the feedback loop is too subtle for our samples. Therefore, it was set to its default value of 5.

On the other hand, the integral gain had not a fixed value. Depending on the sample and the scanned area, its value needed to be adjusted. It was always set to its maximum value before having noise in the outcoming signal. By doing so, the matching between the 'trace' and 'retrace signal' was maximized (quality of the topographical signals too) and noise was avoided.

Finally, the **amplitude setpoint** parameter had also a variable value from one sample to another. Depending on the sample, and even the scanned area of the sample, the oscillation amplitude that the feedback loop tries to maintain constant must be adjusted on a case-by-case basis to be optimal. This parameter is tightly bonded to the integral gain parameter. For instance, when the integral gain is at its maximum value before having noise, lowering the amplitude setpoint will usually induce noise in the signal. The adjustment of these two parameters has thus to be done in parallel.

3.2.5 Conclusion from these results

From Table 3.3 it is obvious that the deposition of the coating on the fabric does not influence the fiber roughness. Moreover, the fiber roughness does not contribute to the fabric roughness. Consequently, the total roughness felt by the water droplet is essentially the macroscale roughness of the fabrics which results from the weave pattern. The hydrophobic properties shown by the fabrics are thus mainly due to the macroscale properties of the fabric.

The observations done based on AFM measurements opens a door for improvement of the hydrophobic properties. Indeed, increasing the microscale fiber roughness by any means would most likely increase the hydrophobic properties of the fabrics even though certain fabrics provide already interesting water-repellent properties with smooth fibers.

3.3 Contact angle measurements and assessment of the water repellency of the coated fabrics

Contact angle, static roll-off angle and dynamic roll-off angle measurements were performed on the different samples with water droplets of 10 μL (detailed procedure in section 2.5). These measurements were performed in order to characterize the influence of the surface texture of the fabrics and the effect of the coating nature on the final water-repellent properties of the coated fabrics. The different results from these measurements are now discussed as well as the observations one can make from them.

3.3.1 Static contact angles

The average static contact angles for each fabric and each coating are given in Table 3.6 and examples of measurements performed on different PDMS-coated fabrics are displayed in Figure 3.12. Furthermore, the standard error (SE) of the average contact angle for each sample is given in the table. As already mentioned, the static contact angles were measured at least at four different locations on the samples. The data presented in the table below are thus the averaged values. Moreover, the static contact angles for the coated silicon wafers are given. These contact angles are equivalent to the Young-Dupré contact angle (θ_Y) as previously explained.

Sample name	PDMS	PM900	SchPFF
Silicon wafer	$113.1^\circ \pm 0.99$	$113.0^\circ \pm 0.69$	$115.3^\circ \pm 0.14$
Fabric1	$131.2^\circ \pm 0.77$	$126.6^\circ \pm 0.73$	$131.3^\circ \pm 0.44$
Fabric2	$130.9^\circ \pm 0.30$	$131.1^\circ \pm 0.39$	$130.1^\circ \pm 0.42$
Fabric3	$138.9^\circ \pm 0.16$	$137.2^\circ \pm 0.29$	$137.7^\circ \pm 0.27$
Fabric4	$136.6^\circ \pm 0.30$	$137.3^\circ \pm 0.32$	$136.4^\circ \pm 0.31$
Fabric7 face A	$136.9^\circ \pm 0.34$	$138.9^\circ \pm 0.28$	$139.7^\circ \pm 0.34$
Fabric7 face B	$139.5^\circ \pm 0.39$	$138.0^\circ \pm 0.27$	$138.1^\circ \pm 0.41$
Fabric5	$139.2^\circ \pm 0.37$	$139.2^\circ \pm 0.38$	$139.7^\circ \pm 0.30$
Fabric6	$140.0^\circ \pm 0.14$	$140.6^\circ \pm 0.32$	$140.2^\circ \pm 0.30$

Table 3.6 – Average contact angles measured for the different coated fabrics and the coated substrates. The associated standard error of each contact angle measurement (computed from at least four different measurements performed at different locations on the sample) is also indicated.

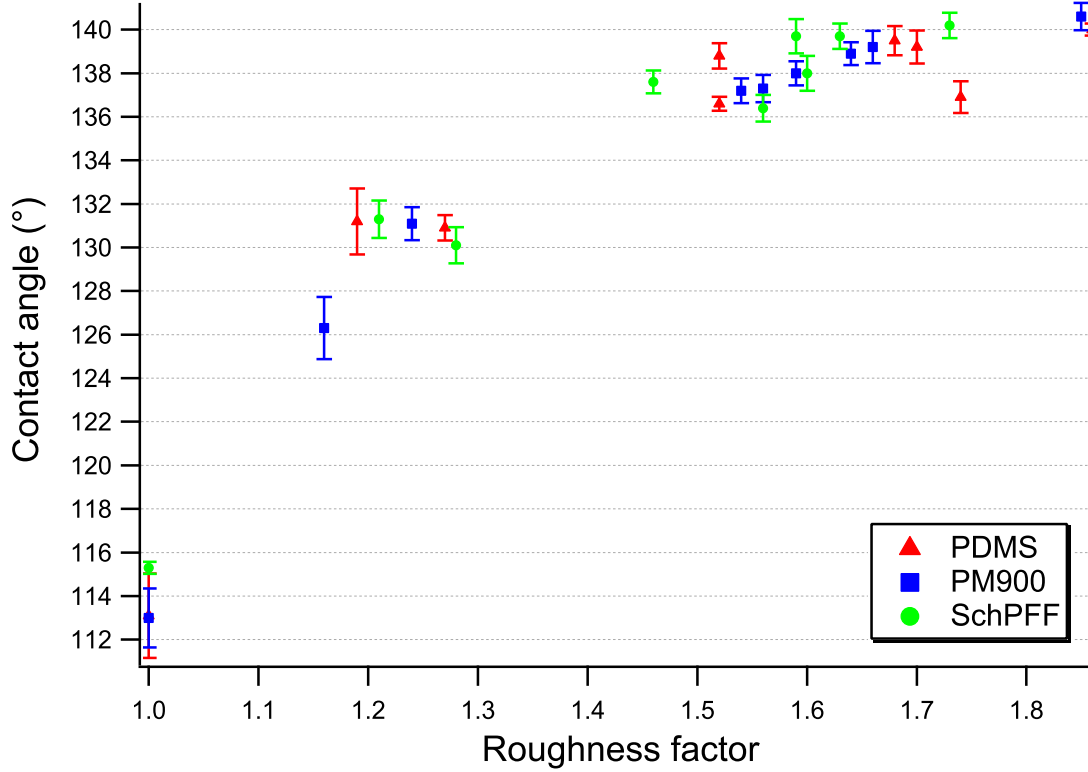


Figure 3.11 – Graphical representation of the variation of the contact angle versus the measured roughness factor for each type of coating (PDMS, PM900 and SchPFF). The values reported on the x axis are the ones presented in Table 3.1 and those of the y axis, their respective contact angle presented in Table 3.6. The error bar represents $1.96 \times SE$ (standard error) where 1.96 is the 0.975 quantile if one assumes the distribution of the contact angles to be normal.

The first observation resulting from this table and the graphical analysis of Figure 3.11 is that the static contact angle increases with increasing roughness. However, this relationship is not linear; it seems that the contact angle reaches a plateau for roughness higher than 1.7 as can be seen in Figure 3.11. The Fabric6 sample exhibits the highest contact angles and has the highest roughness factor too (see Table 3.1) regardless of the coating deposited on its surface. Yet, the Fabric3 sample shows contact angles on the order of 138° , which is close to the highest measured contact angles of the Fabric6 sample. This shows that even less rough samples can present very good water repellency with the used coatings. One may add that the contact angles for the fabrics Fabric7 face A, Fabric7 face B, Fabric5 and Fabric6 might be slightly underestimated. Indeed, when dropping off the water droplet on the surface of these samples, the droplet sometimes stabilized at a position slightly different from the one located vertically under the needle dispensing the droplet. This phenomenon occurred especially for the Fabric6 sample, the most rough of the samples. This is due to fibers sticking out of the surface that the droplet cannot wet. In Figure 3.12h one can clearly see these fibers that stick out from the fabric surface. The droplet is then unstable and therefore, rolls to a more stable position which is necessarily lower than the fibers sticking out of the surface. Since the

droplet is at a lower position than these specific fibers, it is difficult to clearly identify the surface-water interface and consequently to determine accurately the value of the contact angle. For the reason, the baseline delimiting the border between the fabric surface and the water was drawn manually via the software. Since the value of the contact angle is highly dependent on the position of this baseline that is manually indicated, the measurements for rougher surfaces were more prone to experimental errors than the smoother surfaces. Therefore, we think that the measured contact angles for rougher samples are probably slightly underestimated.

The second important observation from Table 3.6 and Figure 3.11 is that the contact angles for the different types of coatings are close to one another for a given fabric. This means that the nature of the coatings does not influence significantly the wettability of the fabric and that the hydrophobic properties of these coatings are quite similar. Therefore, these measurements alone do not provide enough information to classify the different coatings in terms of performance.

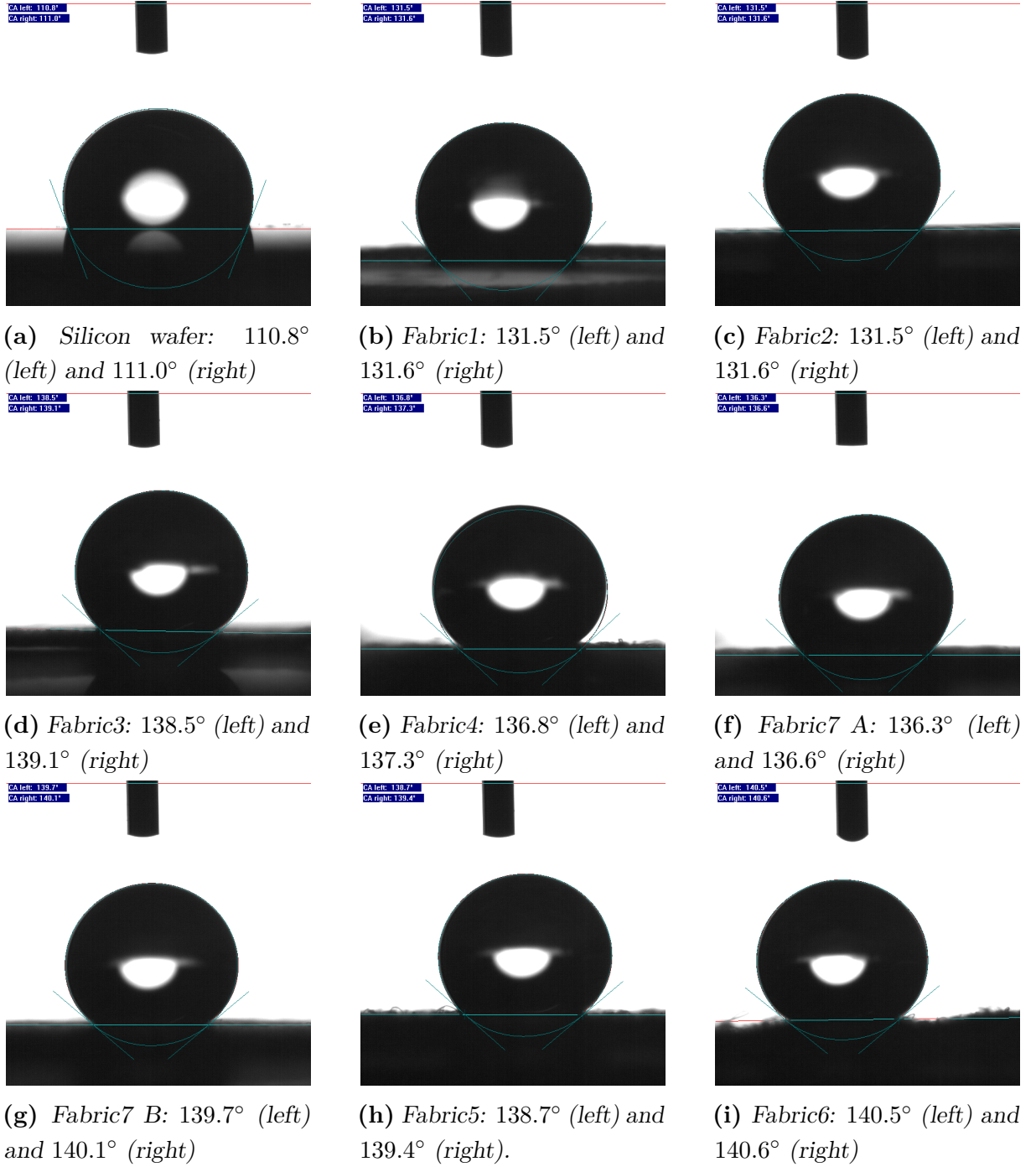


Figure 3.12 – Examples of static contact angle measurements. The samples presented here are all coated with PDMS. The left and right measured contact angles are given in their respective caption.

Wenzel model compared to our measurements

Wenzel described the relationship between the measured contact angle (θ) and Young-Dupré contact angle (θ_Y) in the case of a rough surface that is chemically homogeneous and completely wetted under the water droplet surface (see section 1.2.1). Moreover, to characterize the roughness of the surface, he introduced the roughness factor r (equation 1.1) that we computed for the different samples in Table 3.1. The measured contact angles of the different samples are provided in Table 3.6. The Young-Dupré contact angle is assumed to be equal to the one measured for the coated silicon wafers which are reported in Table 3.5.

To assess if samples exhibit a state comparable to the conditions Wenzel defined, we computed both terms of equation 1.13 for each sample. They are listed in Table 3.7. The results presented in this table show that none of the samples seems to be in the Wenzel state. The difference between both terms might be explained by two assumptions. First, the sample is not in the Wenzel state because air-pockets are trapped underneath the water droplet. In that case, the Cassie-Baxter model is more accurate to determine the relationship between θ and θ_Y .

Second, as discussed in section 3.1.4, because of the used scan rate in the stylus profilometry measurements, the estimation of the roughness factor r might not be suitable for quantitative analyses. Therefore, the difference between the two terms of the equation might also be due to a qualitative and not to a quantitative assessment of the roughness factor. It is therefore difficult to conclude whether (some) samples do or do not exhibit the Wenzel state when a water droplet is deposited on their surface.

Sample name	PDMS		PM900		SchPFF	
	$r \cos \theta_Y$	$\cos \theta$	$r \cos \theta_Y$	$\cos \theta$	$r \cos \theta_Y$	$\cos \theta$
Fabric1	-0.467	-0.659	-0.453	-0.596	-0.517	-0.660
Fabric2	-0.498	-0.655	-0.485	-0.657	-0.547	-0.644
Fabric3	-0.596	-0.754	-0.602	0.734	-0.624	-0.740
Fabric4	-0.596	-0.727	-0.610	-0.735	-0.667	-0.724
Fabric7 face A	-0.671	-0.730	-0.641	-0.754	-0.697	-0.763
Fabric7 face B	-0.659	-0.760	-0.621	-0.743	-0.684	-0.744
Fabric5	-0.667	-0.757	-0.649	-0.757	-0.679	-0.763
Fabric6	-0.730	-0.766	-0.723	-0.773	-0.739	-0.768

Table 3.7 – Comparison of the two terms of the equation Wenzel (equation 1.13) proposed to describe the relationship between the measured contact angle (θ) and Young-Dupré contact angle (θ_Y) in the case of rough surface with homogeneous wetting. The values reported in this table have been computed based on Tables 3.1 and 3.6 for each sample. The contact angles measured on the surface of the silicon wafers are assumed to be equal to θ_Y .

3.3.2 Static roll-off angles

The static roll-off angles were also measured on the different samples in order to further compare the coatings between each other and to evaluate the effect of surface texture on this type of measurement. Table 3.8 summarizes the average static roll-off angle of the different samples and their associated SE. All coated fabrics do not especially have a static roll-off angle. In other words, if the droplet is still stucked on the sample surface when it is tilted at 90° (perpendicular to the floor), we concluded about the absence of a static roll-off angle for such samples. Figure 3.13 presents a graphical analysis of the static roll-off angle measurements by showing the variation of measured static roll-off angle as a function of the roughness of the sample, for each type of coating. Additionally, an exponential fit of the data obtained for each coating was added to this graphic.

Sample name	PDMS	PM900	SchPFF
Fabric1	N/A	N/A	N/A
Fabric2	N/A	N/A	$63.8^\circ \pm 2.9$
Fabric3	$42.0^\circ \pm 2.1$	N/A	$29.0^\circ \pm 3.1$
Fabric4	N/A	N/A	$36.0^\circ \pm 2.2$
Fabric7 face A	$33.5^\circ \pm 0.9$	N/A	$20.0^\circ \pm 1.5$
Fabric7 face B	$32.0^\circ \pm 1.5$	N/A	$22.4^\circ \pm 2.8$
Fabric5	$41.0^\circ \pm 2.3$	N/A	$46.2^\circ \pm 1.4$
Fabric6	$29.7^\circ \pm 3.7$	$51.0^\circ \pm 4.4$	$17.7^\circ \pm 1.4$

Table 3.8 – Average static roll-off angles measured for the different coated fabrics. The associated standard error is added to the given values. For the samples for which the water droplet still sticks at their surface when tilted at 90° , the symbol 'N/A' is used.

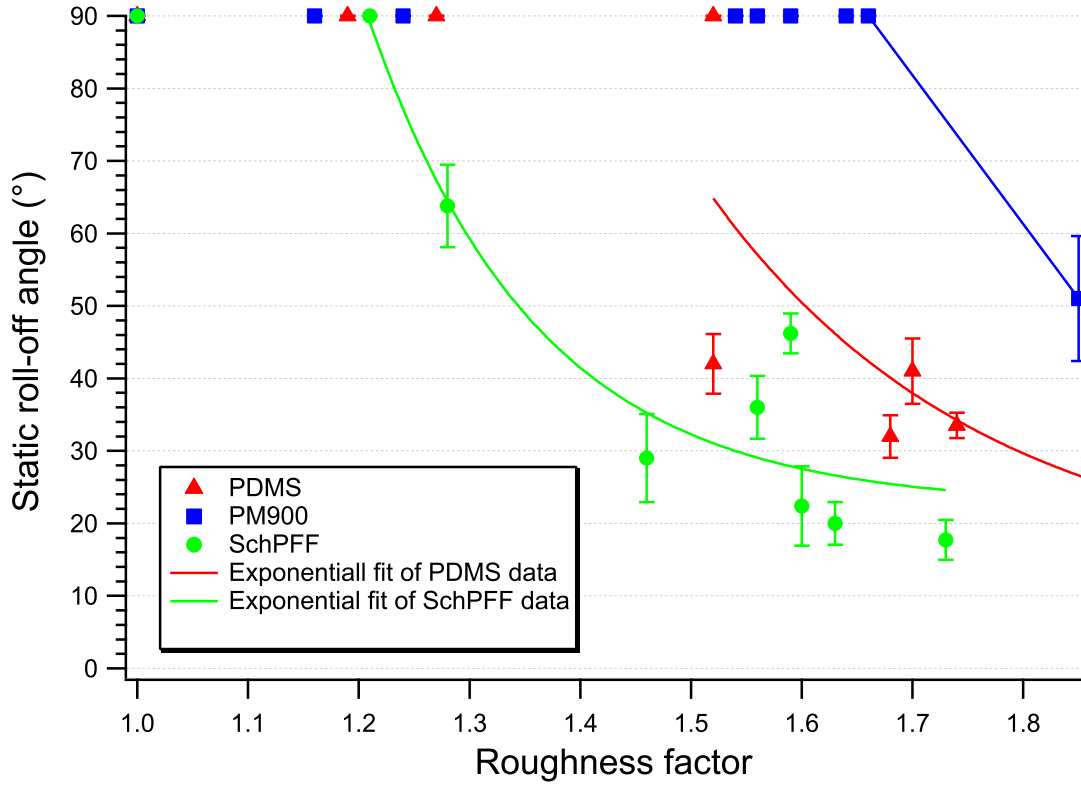


Figure 3.13 – Variation of the static roll-off angle versus the surface roughness for the samples coated with the three different formulations. The values reported on the x axis are the ones presented in Table 3.1 and those reported on the y axis, their respective static roll-off angle presented in Table 3.8. The error bar represents $1.96 \times SE$ (standard error) where 1.96 is the 0.975 quantile if one assumes the distribution of the static roll-off angles to be normal. An exponential fit of the data is also added to the graph for the coatings PDMS and SchPFF. For a given coating, this fit is delimited by the last measurement for which no static roll-off angle was obtained and the lowest measured static roll-off angle.

In contrast to the measurements of the contact angles, the different coatings do not exhibit similar properties for a given fabric regarding the static roll-off angle measurements. The coating SchPFF provides the best water-repellent performances to the fabrics independently of their roughness as clearly shown in Figure 3.13. However, it is obvious from the graphical analysis that a sample needs a minimal roughness to get a static roll-off angle. This critical roughness varies from one coating to the other. The coating PM900 clearly presents the poorest properties regarding this type of measurement. Only the roughest sample (Fabric6) shows a static roll-off angle with this coating. As for the PDMS coating, it confers to the fabrics properties in-between the ones of PM900 and SchPFF.

The second important observation from the obtained data is that the static roll-off angle decreases with increasing roughness. This observation is valid for all types of coatings and independent of their nature. Hence, the higher the roughness of fabrics, the lower the wettability (higher contact angle), the lower the static roll-off angle. This means that

increasing the roughness increases more the water repellency of the fabric than it hinders the droplet to roll-off. The question arising from this observation is to know whether or not there is a limiting surface roughness where the measured static roll-off angle would increase again.

3.3.3 Dynamic roll-off angles

The last type of characterization performed to assess the water repellent properties of the samples was the measurement of the dynamic roll-off angles. Table 3.9 summarizes the intervals obtained for each coated fabrics. For the smallest angle of the given interval, the water droplet barely rolled-off or still stucked to the surface while for the largest, the droplet always rolled-off, and this at different locations on the sample. In other words, the given interval contains the value of the dynamic roll-off angle at any given place of the sample. As for the static roll-off angle measurement, some samples do not exhibit dynamic roll-off angles, namely the Fabric1 and Fabric2 samples coated with PDMS and PM900.

Sample name	PDMS	PM900	SchPFF
Fabric1	N/A	N/A	50°~55°
Fabric2	N/A	N/A	40°~50°
Fabric3	20°~30°	25°~30°	15°~20°
Fabric4	50°~55°	35°~40°	20°~30°
Fabric7 face A	20°~25°	18°~22°	10°~15°
Fabric7 face B	15°~25°	15°~20°	10°~15°
Fabric5	20°~25°	20°~30°	25°~30°
Fabric6	5°~15°	5°~10°	5°~10°

Table 3.9 – *Intervals of dynamic roll-off angles measured for the coated fabrics. The symbol 'N/A' is used for the samples for which no dynamic roll-off angle was measured when they were tilted at 80° (maximum possible angle to perform the dynamic roll-off angle measurement).*

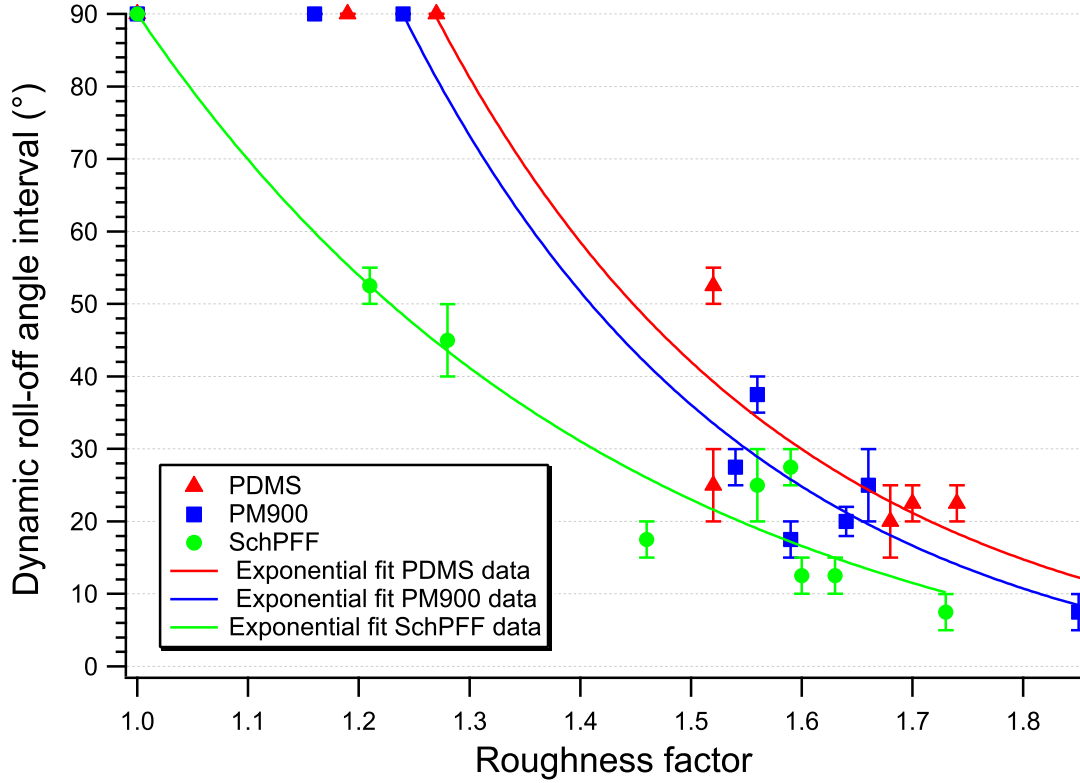


Figure 3.14 – Interval of the dynamic roll-off angle versus the surface roughness for the samples coated with the three different formulations. The values reported on the x axis are the ones presented in Table 3.1 and those reported on the y axis, their respective dynamic roll-off angle presented in Table 3.9. The error bar represents the interval that should contain the dynamic roll-off angle at any given place of the sample. An exponential fit of the data is also added to the graph for the three coatings (PDMS, PM900 and SchPFF). For a given coating, this fit is delimited by the last measurement for which no dynamic roll-off angle was obtained and the lowest measured dynamic roll-off angle.

As expected from the previous observations of the two other types of measurements, the dynamic roll-off angle decreases with increasing roughness for the three types of coatings. Again, increasing the roughness increases more the water repellency than it prevents water to roll-off on the fabric. One may also wonder if a critical roughness would exist for which the dynamic roll-off angle would increase because the surface roughness would pin the droplet. Yet, from our data, we can only say that increasing the roughness increases the water repellency and reduces the two types of roll-off angles.

Similarly to the static roll-off angles, the different coatings induce different ranges of dynamic roll-off angles for a given fabric. The coating SchPFF provides the lowest dynamic roll-off angles whereas the PDMS and PM900 coatings show similar properties. As for the static roll-off angle measurements, the coating SchPFF exhibits the best hydrophobic properties. A critical roughness is also necessary for the fabric to present a dynamic roll-off angle. This one is particularly low for the SchPFF coating.

3.3.4 Conclusion about the obtained results

The three types of measurements, i.e., the contact angle, the static roll-off angle and the dynamic roll-off angle measurements, are complementary and allowed us to draw several conclusions regarding the effect of the surface roughness and of the coating nature on the water-repellent properties of the fabrics. The first one is that increasing the roughness enhances the water repellency as predicted from the models presented in section 1.2.1 and this, regardless of the type of coating. For each coating and each type of measurement, the performances of the samples are improved with an increasing roughness. Therefore, an efficient water repellency is inseparable of a certain surface roughness. What is interesting is that samples such as the Fabric3 sample ($r \sim 1.5$) present contact angles almost as high as the Fabric6 sample ($r \sim 1.8$) though, for this sample, they are probably slightly underestimated. One has to keep in mind that none of these fabrics present a microscale roughness. Therefore, there is room for to improve the water repellency of these fabrics by providing them a microscale roughness with an additional treatment.

Secondly, the coating nature has an obvious influence on the roll-off angle of water droplets. Though from the static contact angle measurements the three types of coatings seemed to be equivalent in terms of water repellency, the static and dynamic roll-off angles revealed the SchPFF coating to be more effective than the others. In both cases, this water-based emulsion of paraffin particles with an added melamine resin allows water to roll-off more easily on the fabric even for samples of lower roughness compared to the two other coatings. The SchPFF is thus more attractive in this respect.

Conclusions

The importance of surface roughness and its influence on the interactions of a solid surface with its surroundings was first highlighted in this master thesis. Numbers of different roughness parameters have therefore been developed to describe as precisely as possible the roughness of a random solid surface. In the case of this study, we chose to describe the surface roughness with the roughness factor r , defined by Wenzel, and to calculate it from data obtained by stylus profilometry and Atomic Force Microscopy. Afterwards, the measurements of the contact angles, the static and the dynamic roll-off angles allowed us to evaluate the water repellency of each coated fabric. These last measurements also enabled us to correlate the roughness and the final hydrophobic properties shown by the fabrics and to compare the performances of the different coatings. To do so, seven different fabrics were used. Their respective roughness ranged from $r = 1.16$ to $r = 1.86$. Additionally, three commercial formulations were used to prepare the three different coatings. The prepared coatings were made from two fluor-free formulations (PDMS and SchPFF) and one formulation made of a short chain (C4) perfluorinated compound (PM900).

First, stylus profilometry provided three-dimensional images with high vertical resolution (less than 1 nm) and allowed us to scan large surface areas and is thus an attractive technique to image fabrics at the macroscale. However, the lateral resolution is limited by the tip radius. The diameter of the fibers being *ca.* 10 μm and the one of the tip being 1.4 μm , the lateral resolution provided with such a tip was considered as sufficient. At first, scanning the fabrics with a stylus profilometer revealed final images with important misalignments and some glitches. The cheap and efficient solution we found to avoid misalignment of the parallel line profiles building up the three-dimensional scan, simply consists of sticking a smooth and thin tape on the top of the fabric surface and of orientating the sample in such a way that each line profile starts on the tape. As for glitches, these are mainly due to loose fibers sticking to the tip and so far no solution has been found to avoid them, without altering the fabric surface. However, wide scans could possibly locate areas comprising less glitches but this method is time consuming. The scans obtained with the solution using the tape need to be reframed and to undergo mathematical treatment (flattening and deglitching) before computing the roughness factor r from these images. The values obtained for the different fabrics ranged from $r = 1.16$ to $r = 1.86$ and showed that the compared fabrics have quite different surface

textures. From these results, a variation of r smaller than 10% between identical fabrics was observed for the different samples but was not correlated to the deposition of a specific coating onto their surface. These variations are most certainly due to the variable intrinsic properties of a given fabric. Indeed, their production method cannot ensure the fabric to have identical properties for every square millimeter of the fabric surface. Lastly, the problems encountered to compute the roughness factor of Fabric7 face A sample led us to perform a scan at a very slow scanning speed. The resulting roughness factor was much higher than all previous measurements ($r = 2.05$). Therefore, it seems that the obtained roughness factor is dependent on the scanning speed, and therefore provides only a qualitative estimation for this parameter which is suitable to compare samples between each other but not to perform quantitative comparisons, for instance, to check if samples are in the Wenzel state.

Second, by means of AFM, we measured roughness features at the surface of the fibers of the fabrics, which allowed us to compute the roughness factor at the microscale. These measurements revealed extremely small features and the resulting roughness factor $r \simeq 1$ obtained for all types of fabrics led us to conclude that the fabrics do not exhibit a microscale roughness. The Fabric6 sample was harder to scan because of loose fibers sticking out and the important height disparities of the surface (roughest sample). Approaching the tip and precisely scanning the fibers appeared to be challenging and the measurements were probably not as accurate as for the other fabrics. In addition, silicon wafers coated with the three hydrophobic formulations were measured by AFM and the computed roughness factor was equal to one. These samples could thus be used to measure the contact angle on a completely flat and chemically homogeneous surface, since the silicon wafers were spin-coated with the three different formulations. In other words, we assumed these samples to fulfill the conditions of the Young-Dupré model and that the contact angles measured on these surfaces were equal to the Young-Dupré contact angle, θ_Y , for the studied coatings. This specific contact angle is generally used as a reference in other models describing the interaction of a surface with water. Indeed, these alternative models tend to correlate the measured contact angle θ and the Young-Dupré contact angle θ_Y , which explains the importance of evaluating this specific contact angle.

Finally, the study of the variation of the contact angle versus the surface roughness, evidenced that the larger the roughness, the higher the water repellency. Yet, this relationship is not linear since for samples with large roughness, the difference between their average contact angle is quite small. The highest contact angles were observed for the roughest studied fabric, the Fabric6 sample, with contact angles of about 140° . The high contact angles obtained for the rougher samples showed satisfying water-repellent properties for fabrics only by modifying their surface energy by depositing a coating onto their surface. Yet, an important observation has to be kept in mind regarding the static contact angle measurements. It is hard to precisely determine the boundary between the water droplet and the fabric surface for rougher samples. Since the determination of the

contact angle is sensitive to the position of this boundary, the accuracy of the measurements inevitably decreases for rougher samples. For these fabrics (Fabric5, 6 and 7), the water droplet deposited on their surface had a tendency to stabilize at points next to the initial location of deposition. This is due to fibers sticking out of the surface that the droplet cannot wet and the droplet has thus to roll at a more stable position which is necessarily lower than the fibers sticking out of the surface. These fibers thus hide the true boundary between the water droplet and the surface from the camera. Therefore, the contact angles measured for rougher surfaces might be slightly underestimated. As for the coatings of different natures, no significant difference appeared in the measured contact angles. The fabrics had similar contact angles regardless of the coating deposited on their surface.

The static and dynamic roll-off angle measurements confirmed the observations made for the contact angles: the rougher the sample, the higher its water repellency, the smaller its static and dynamic roll-off angles. In contrast to the contact angle measurements, a noticeable difference was observed in the roll-off angle results depending on the coating nature. Indeed, with the coating SchPFF the lowest static and dynamic roll-off angles were obtained, whatever the used fabric. Moreover, samples of lower roughness revealed static and dynamic roll-off angles when coated with SchPFF in contrast to the two other studied coatings. Regarding the static roll-off angle, the coating PDMS provided performances in-between the ones of the coatings SchPFF and PM900. For the dynamic roll-off angles, the PDMS and PM900 coatings had similar performances. The coating nature thus clearly affects the performances of the different samples concerning water repellency although the measurements of the contact angles did not revealed it in the first place.

In conclusion, this study revealed that fabrics with a similar surface energy which is determined by the coating applied on their surface, present better water-repellent properties for rougher fabrics. Indeed, it is important to notice that only the choice of an appropriate weave pattern with a defined roughness is enough to provide desired hydrophobic properties (after coating). This was assessed by higher contact angles and lower static and dynamic roll-off angles measured on rougher samples. The measured contact angles already revealed high water repellency for the coated fabrics with a higher roughness factor. Since the total roughness of the studied samples appeared to be caused only by macroscale features, it should be possible to increase the hydrophobic even more properties by giving a microscale roughness to the fabrics. Indeed, from our measurements, fibers did not show roughness features capable of enhancing the total roughness. The door is thus open to get even better hydrophobic properties for textiles.

As for the coating nature, contact angle measurements did not reveal important differences between the three types of coatings. However, the wax-type coating, i.e., the coating SchPFF, showed lower static and dynamic roll-off angles than the PM900 and PDMS coatings when deposited on similar fabrics. Moreover, fabrics of lower roughness presented static and dynamic roll-off angles when coated with SchPFF in contrast to the two other

coatings. If one had to classify these coatings in terms of performance, the coating SchPFF would be the best, followed by the coating PDMS and PM900. Somehow, sailors of the 15th century already had advanced ideas in order to provide their clothes water-repellent properties.

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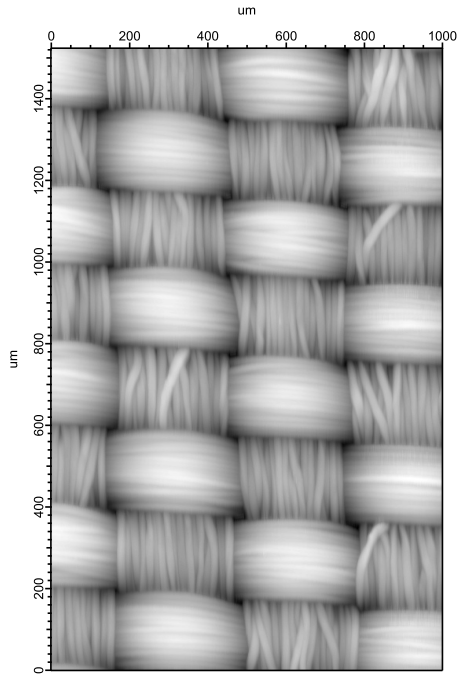
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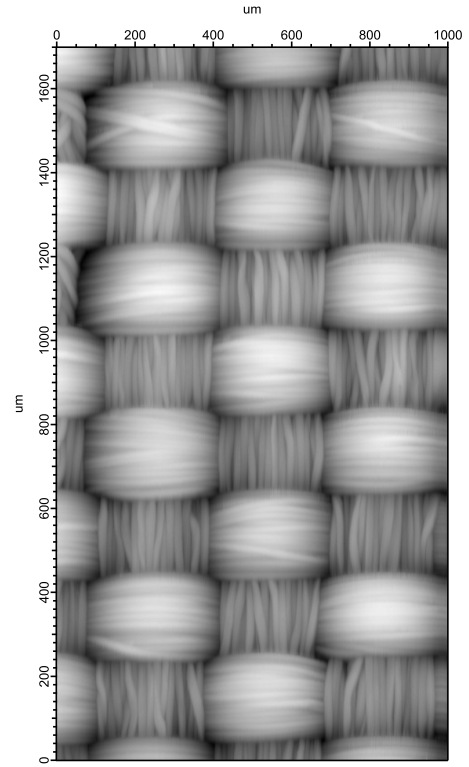
Appendices

Appendix A

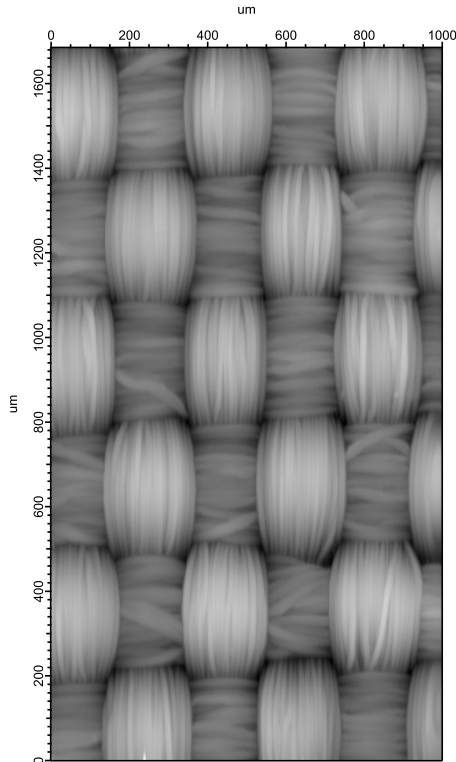
Stylus profilometry images obtained
for the different fabrics



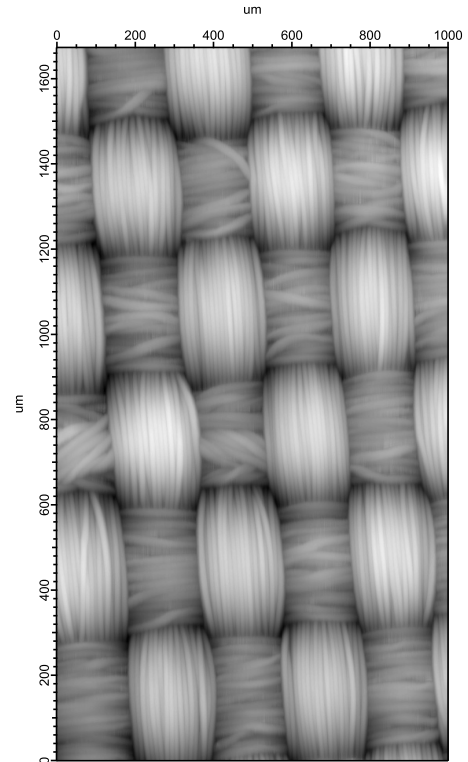
(a) *Fabric1 without any coating.*
Greyscale ranges from 0 to 72 μm .



(b) *Fabric1 coated with PDMS.*
Greyscale ranges from 0 to 82 μm .

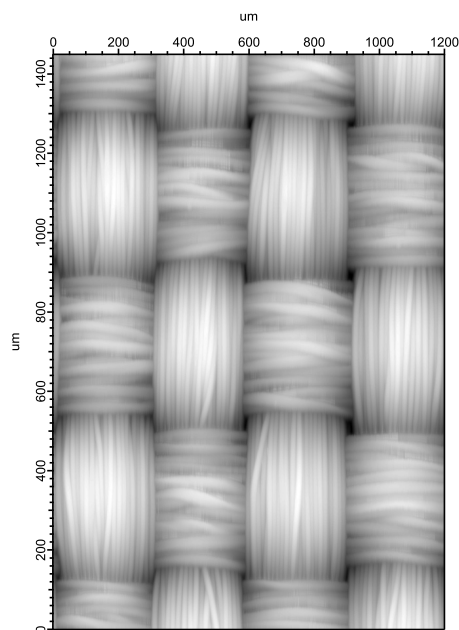


(c) *Fabric1 coated with PM900.*
Greyscale ranges from 0 to 81 μm .

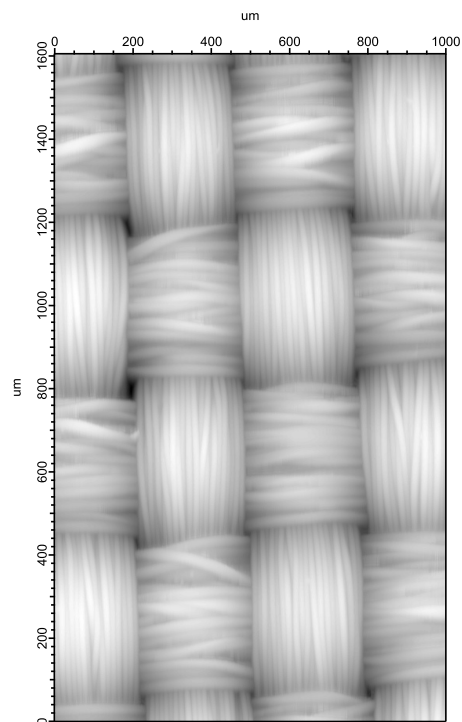


(d) *Fabric1 coated with SchPFF.*
Greyscale ranges from 0 to 78 μm .

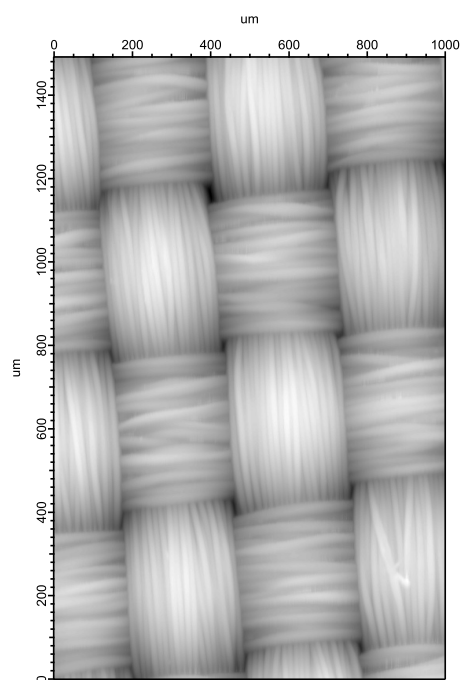
Figure A.1 – *Fabric1 samples imaged by stylus profilometry.*



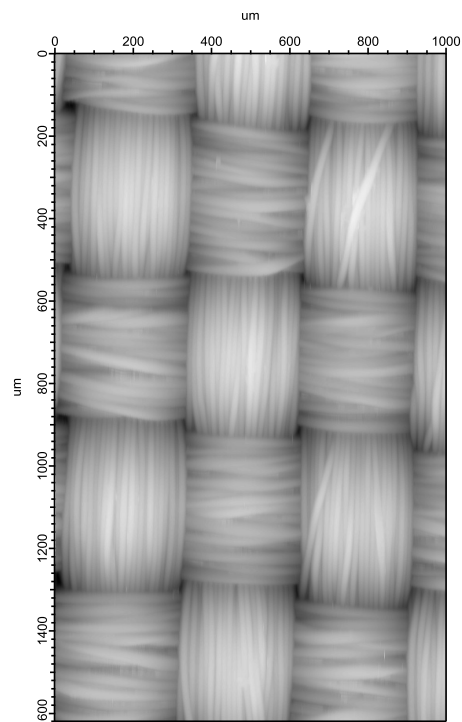
(a) *Fabric2 without any coating. Greyscale ranges from 0 to 105 μm .*



(b) *Fabric2 coated with PDMS. Greyscale ranges from 0 to 129 μm .*

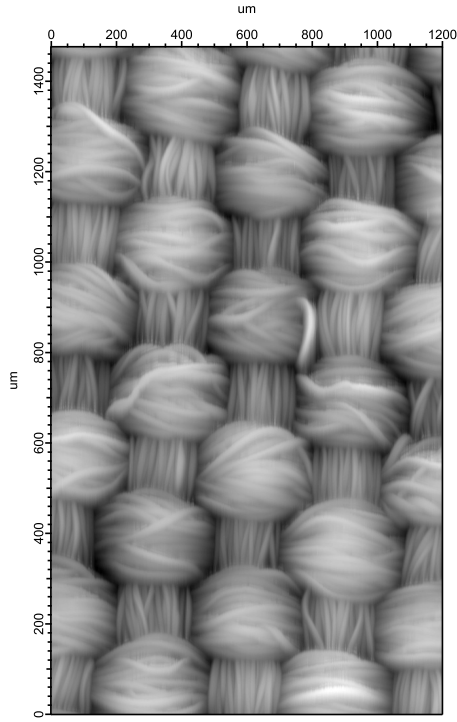


(c) *Fabric2 coated with PM900. Greyscale ranges from 0 to 124 μm .*

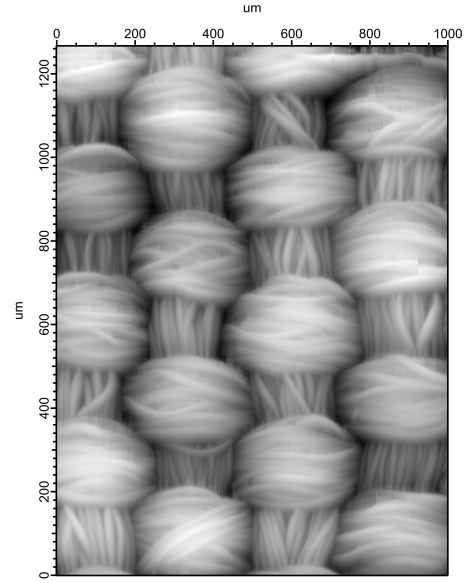


(d) *Fabric2 coated with SchPFF. Greyscale ranges from 0 to 130 μm .*

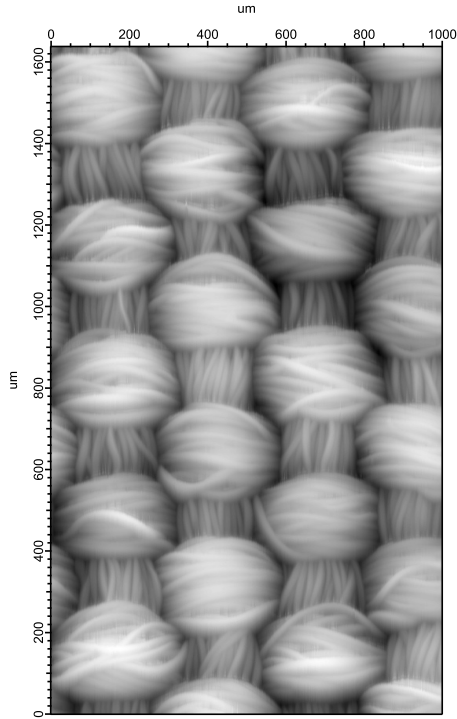
Figure A.2 – *Fabric2 samples imaged by stylus profilometry.*



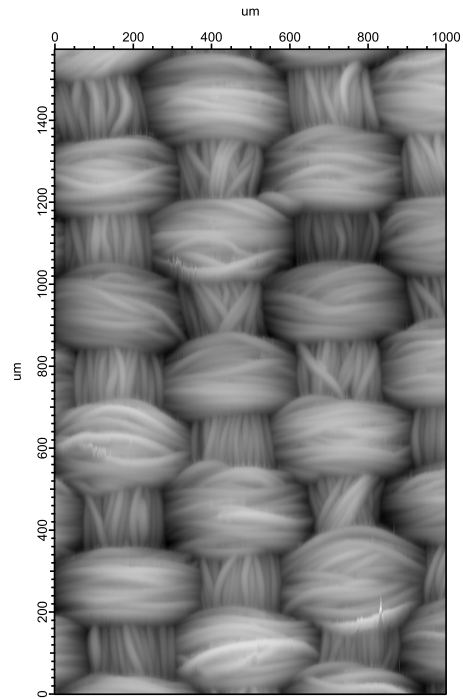
(a) *Fabric3 without any coating.*
Greyscale ranges from 0 to 126 μm .



(b) *Fabric3 coated with PDMS.*
Greyscale ranges from 0 to 136 μm .



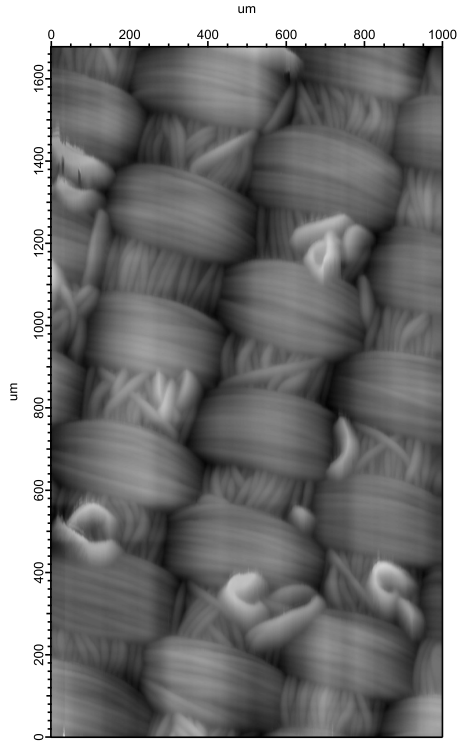
(c) *Fabric3 coated with PM900.*
Greyscale ranges from 0 to 151 μm .



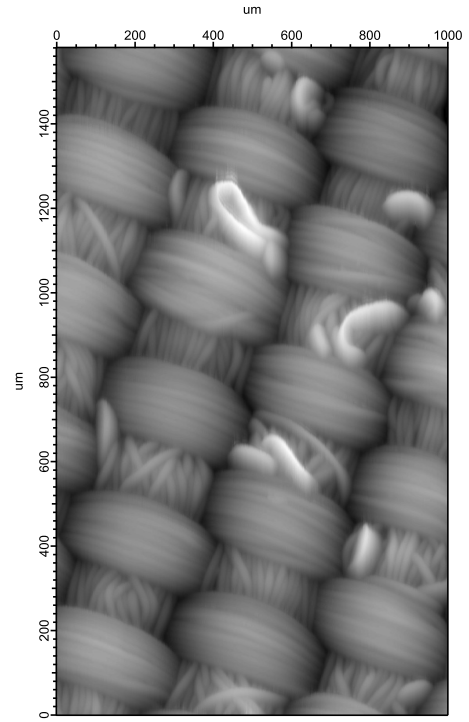
(d) *Fabric3 coated with SchPFF.*
Greyscale ranges from 0 to 141 μm .

Figure A.3 – *Fabric3 samples imaged by stylus profilometry.*

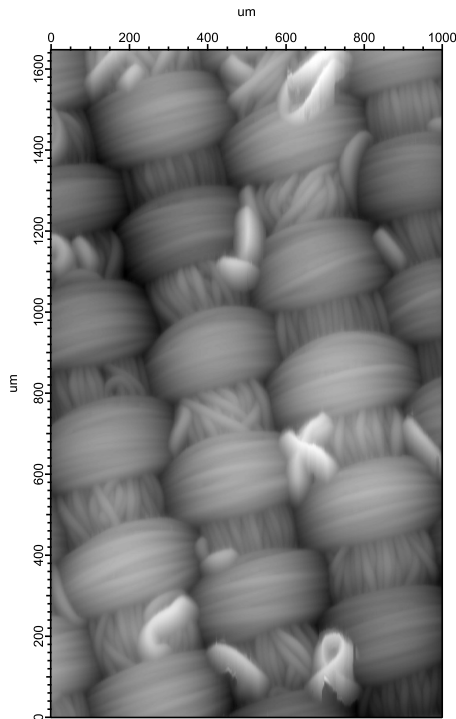
APPENDIX A. STYLUS PROFILOMETRY IMAGES OBTAINED FOR THE DIFFERENT FABRICS



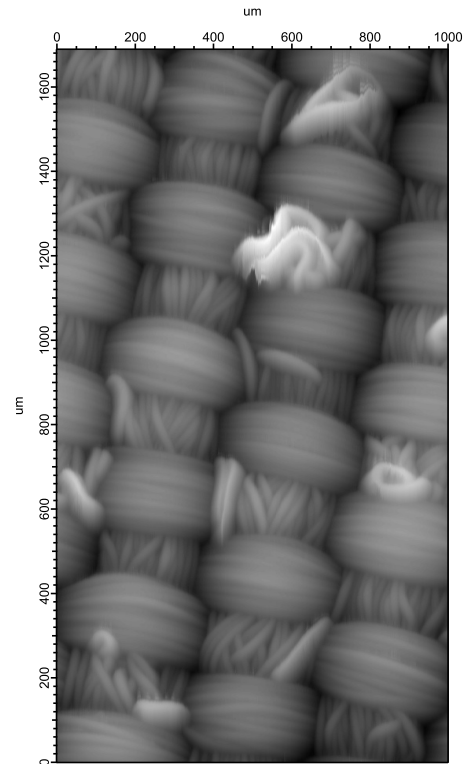
(a) *Fabric4 without any coating.*
Greyscale ranges from 0 to 206 μm .



(b) *Fabric4 coated with PDMS.*
Greyscale ranges from 0 to 212 μm .

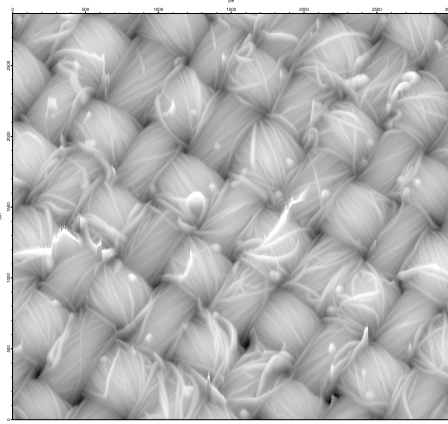


(c) *Fabric4 coated with PM900.*
Greyscale ranges from 0 to 242 μm .

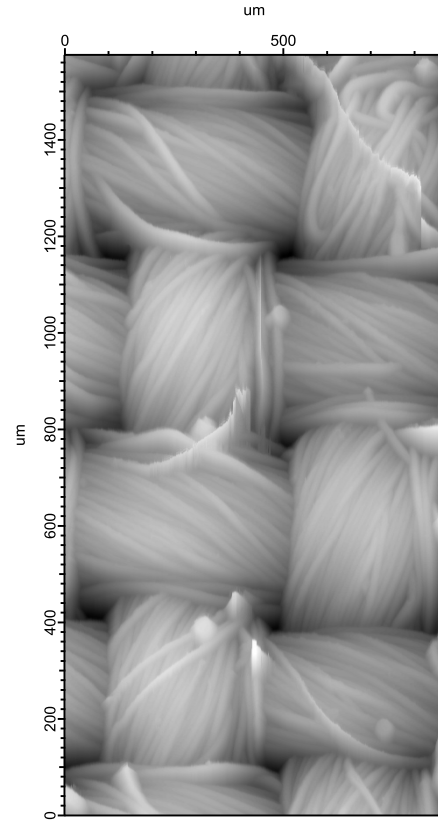


(d) *Fabric4 coated with SchPFF.*
Greyscale ranges from 0 to 256 μm .

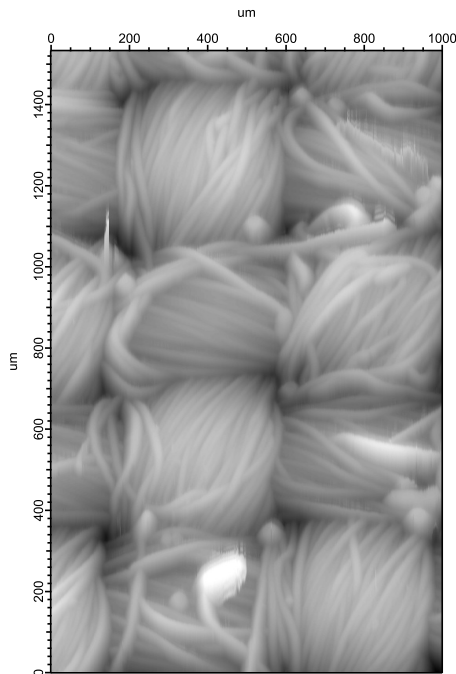
Figure A.4 – *Fabric4 samples imaged by stylus profilometry.*



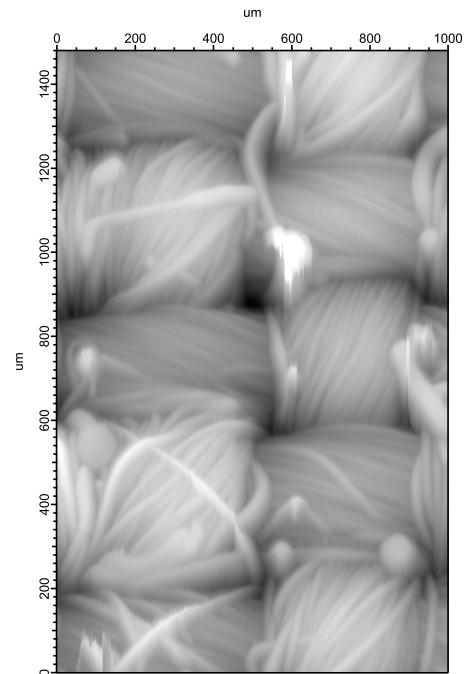
(a) *Fabric5 without any coating.*
Greyscale ranges from 0 to 321 μm .



(b) *Fabric5 coated with PDMS.*
Greyscale ranges from 0 to 260 μm .



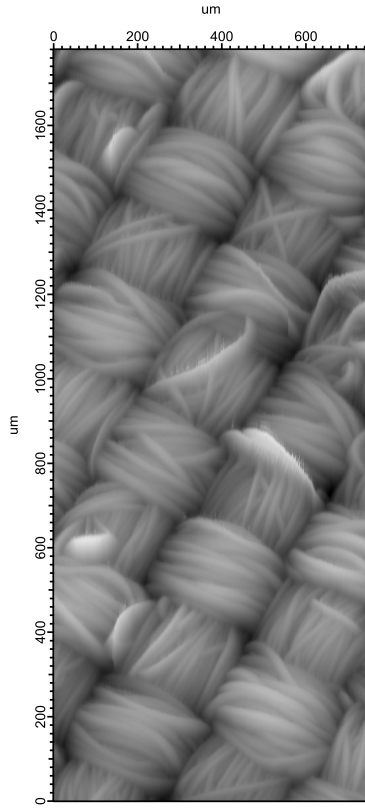
(c) *Fabric5 coated with PM900.*
Greyscale ranges from 0 to 267 μm .



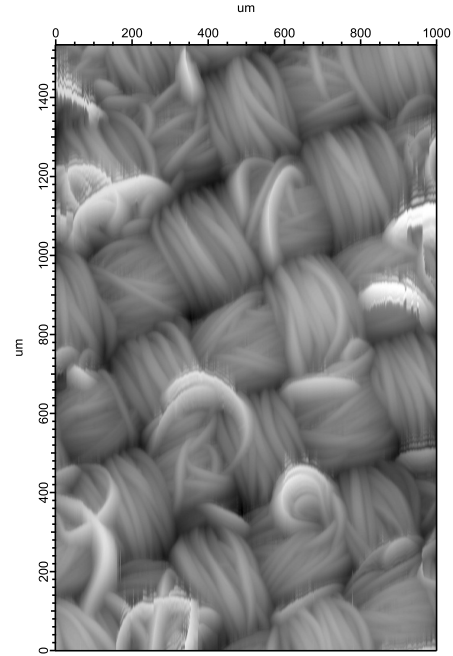
(d) *Fabric5 coated with SchPFF.*
Greyscale ranges from 0 to 266 μm .

Figure A.5 – *Fabric5 samples imaged by stylus profilometry.*

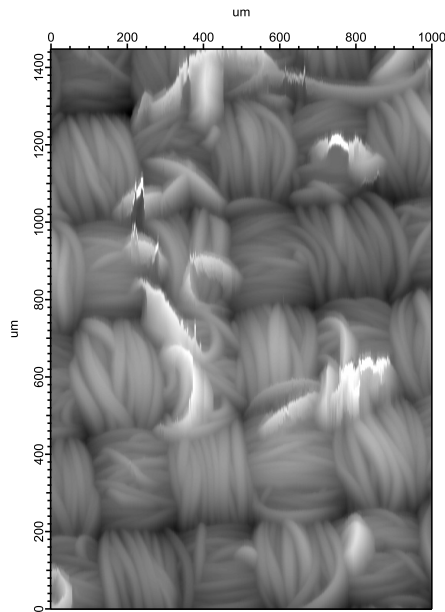
APPENDIX A. STYLUS PROFILOMETRY IMAGES OBTAINED FOR THE DIFFERENT FABRICS



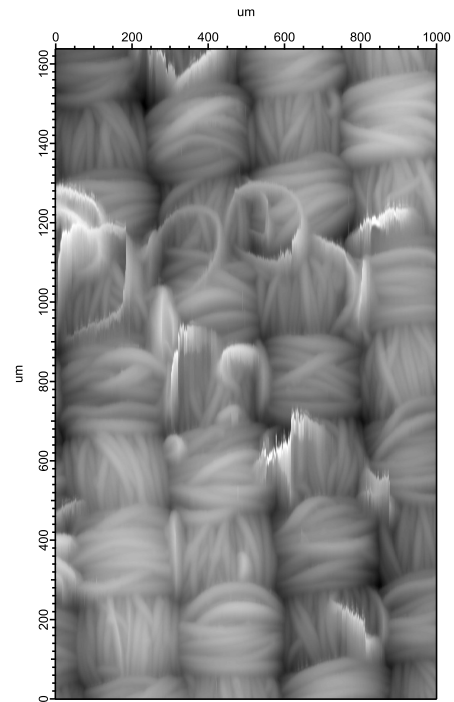
(a) *Fabric6 without any coating. Greyscale ranges from 0 to 245 μm .*



(b) *Fabric6 coated with PDMS. Greyscale ranges from 0 to 246 μm .*

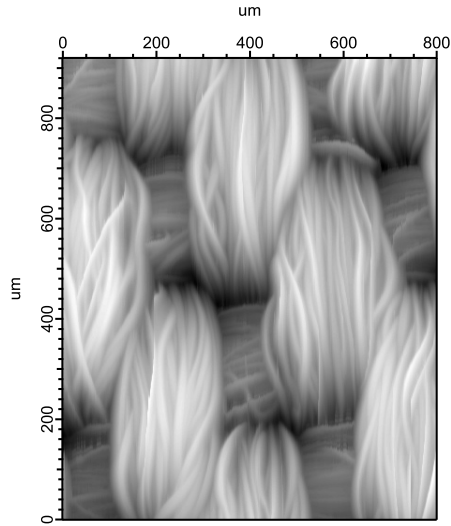


(c) *Fabric6 coated with PM900. Greyscale ranges from 0 to 278 μm .*

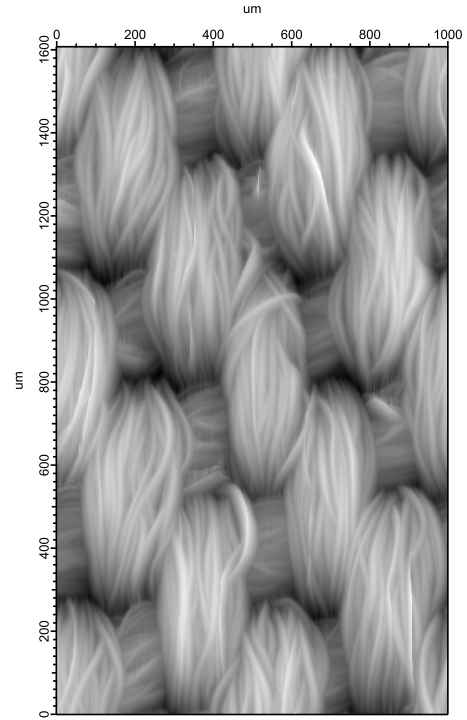


(d) *Fabric6 coated with SchPFF. Greyscale ranges from 0 to 252 μm .*

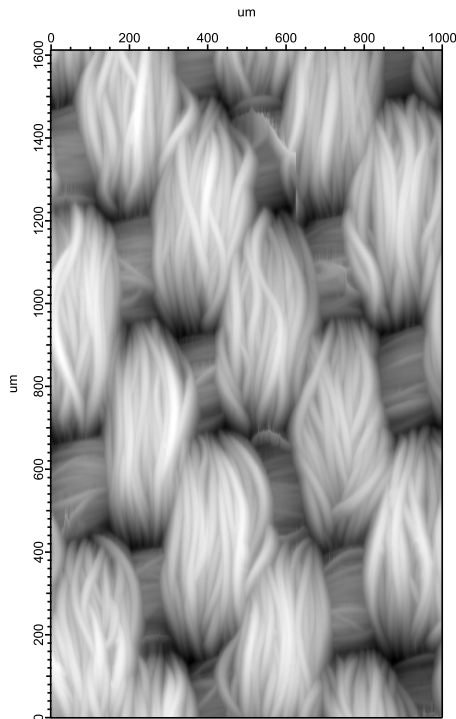
Figure A.6 – *Fabric6 samples imaged by stylus profilometry.*



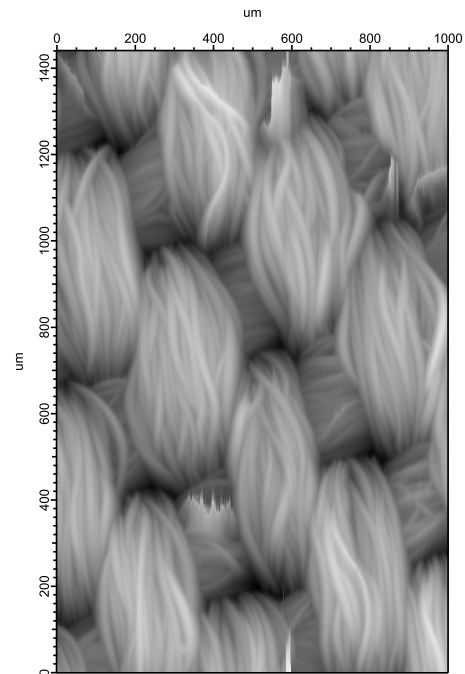
(a) *Fabric7 face A without any coating. Greyscale ranges from 0 to 158 μm .*



(b) *Fabric7 face A coated with PDMS. Greyscale ranges from 0 to 214 μm .*

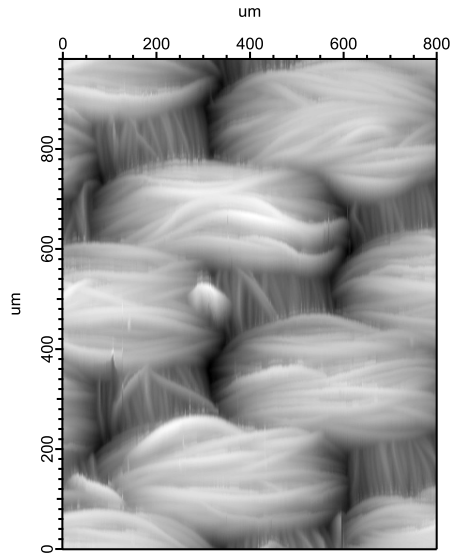


(c) *Fabric7 face A coated with PM900. Greyscale ranges from 0 to 173 μm .*

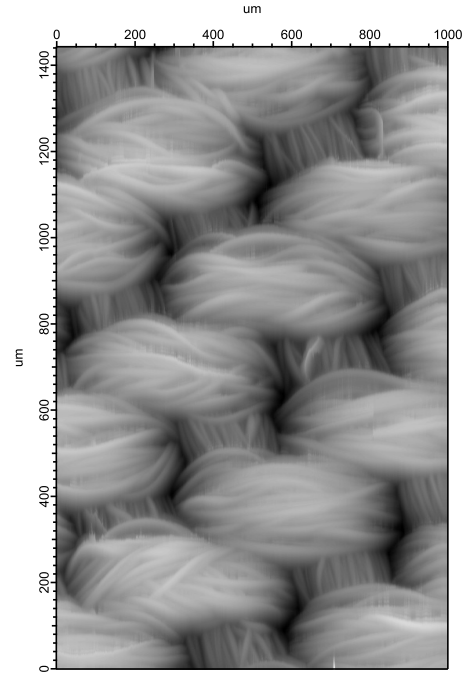


(d) *Fabric7 face A coated with SchPFF. Greyscale ranges from 0 to 207 μm .*

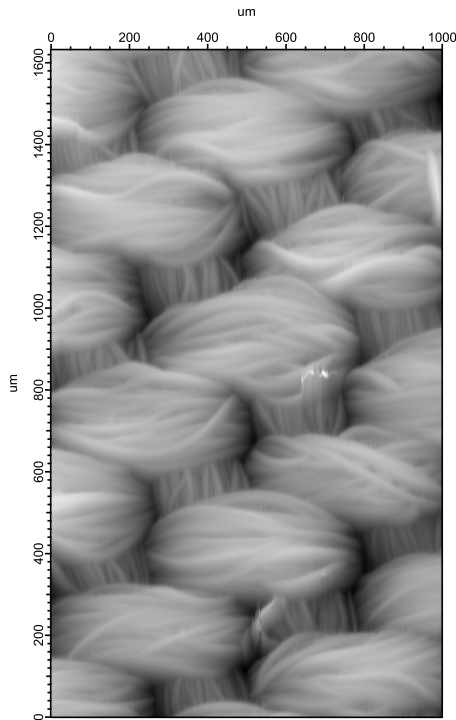
Figure A.7 – *Fabric7 face A samples imaged by stylus profilometry with the scanning direction parallel to the weft yarns sticking out of the surface.*



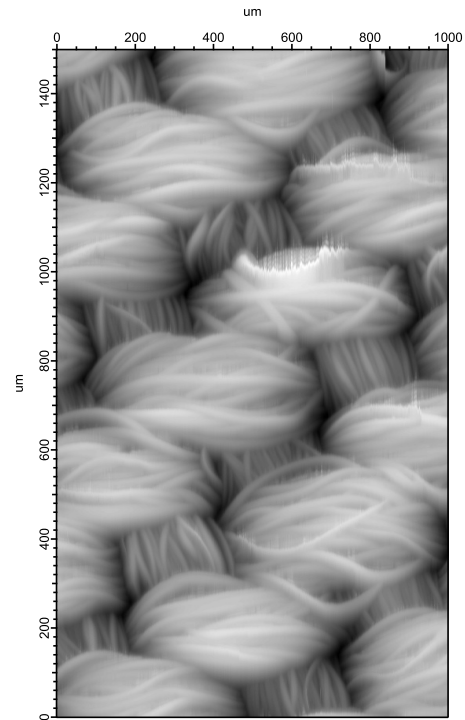
(a) *Fabric7 face A without any coating. Greyscale ranges from 0 to 164 μ m.*



(b) *Fabric7 face A coated with PDMS. Greyscale ranges from 0 to 249 μ m.*

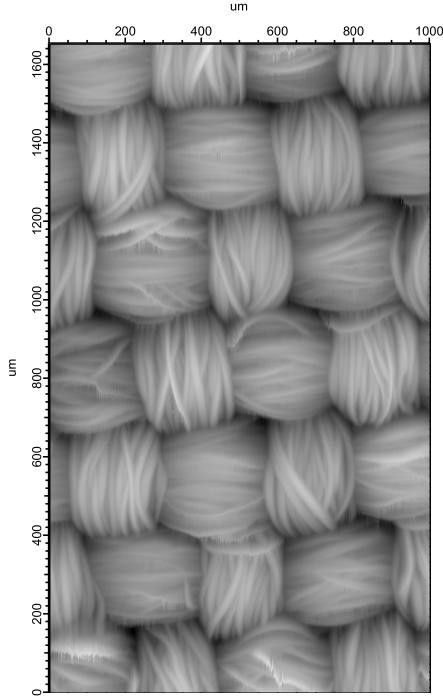


(c) *Fabric7 face A coated with PM900. Greyscale ranges from 0 to 223 μ m.*

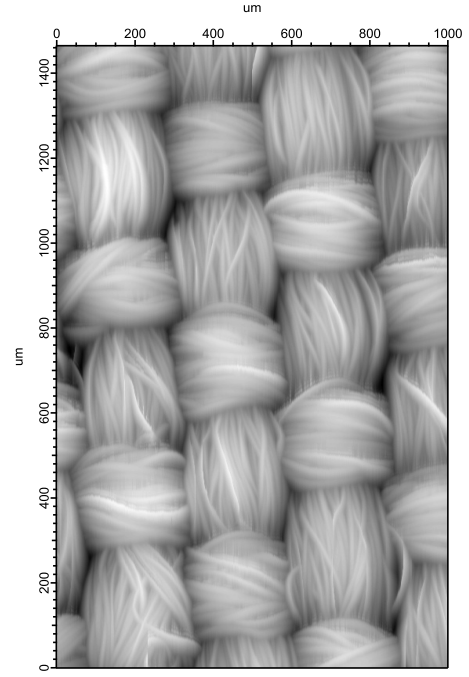


(d) *Fabric7 face A coated with SchPFF. Greyscale ranges from 0 to 181 μ m.*

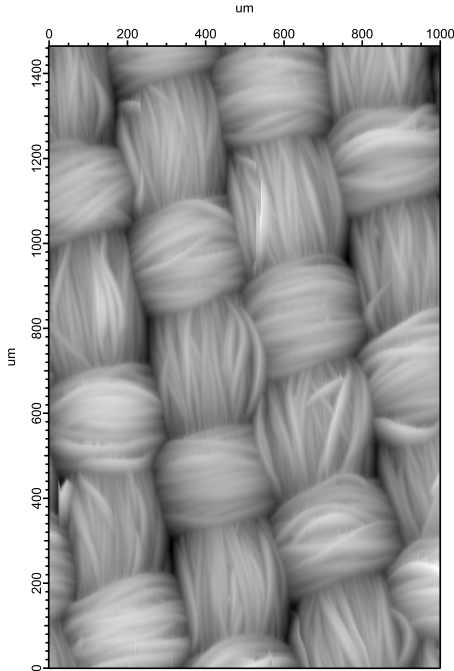
Figure A.8 – *Fabric7 face B samples imaged by stylus profilometry with the scanning direction perpendicular to the weft yarns sticking out of the surface.*



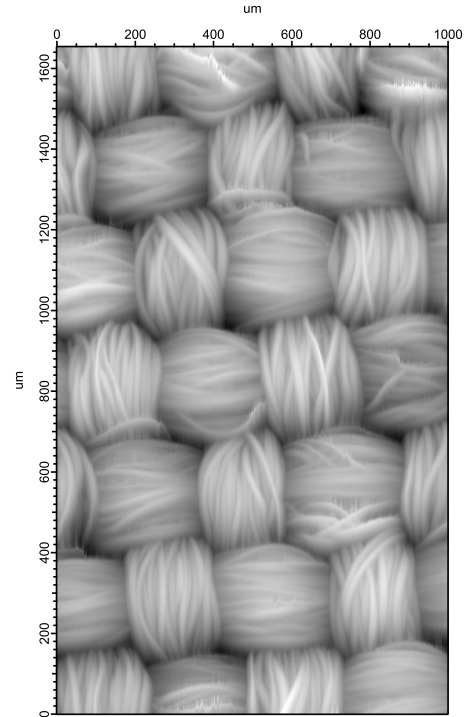
(a) *Fabric7 face B without any coating. Greyscale ranges from 0 to 187 μm .*



(b) *Fabric7 face B coated with PDMS. Greyscale ranges from 0 to 163 μm .*



(c) *Fabric7 face B coated with PM900. Greyscale ranges from 0 to 173 μm .*



(d) *Fabric7 face B coated with SchPFF. Greyscale ranges from 0 to 162 μm .*

Figure A.9 – *Fabric7 face B samples imaged by stylus profilometry.*

Appendix B

AFM measurements and resulting roughness factors

B.1 Roughness factors obtained for the fiber scans from the AFM measurements

	Uncoated	PDMS	PM900	SchPFF
Fabric1	1.01	1.00	1.01	1.01
	1.00	1.01	1.01	1.00
	1.00	1.00		1.00
Average r	1.00	1.00	1.01	1.01

Table B.1 – Roughness factors computed for the scans performed by AFM for the sample *Fabric1* and the resulting average roughness factor.

	Uncoated	PDMS	PM900	SchPFF
Fabric2	1.01	1.01	1.00	1.00
	1.01	1.00	1.01	1.01
	1.01		1.01	1.00
Average r	1.01	1.00	1.01	1.00

Table B.2 – Roughness factors computed for the scans performed by AFM for the sample *Fabric2* and the resulting average roughness factor.

	Uncoated	PDMS	PM900	SchPFF
Fabric3	1.00	1.00	1.00	1.00
	1.00	1.01	1.01	1.00
Average r	1.00	1.00	1.00	1.00

Table B.3 – Roughness factors computed for the scans performed by AFM for the sample *Fabric3* and the resulting average roughness factor.

	Uncoated	PDMS	PM900	SchPFF
Fabric4	1.01	1.01	1.00	1.01
	1.01	1.00	1.00	1.03
	1.00	1.00		1.00
Average r	1.01	1.00	1.00	1.01

Table B.4 – Roughness factors computed for the scans performed by AFM for the sample *Fabric4* and the resulting average roughness factor.

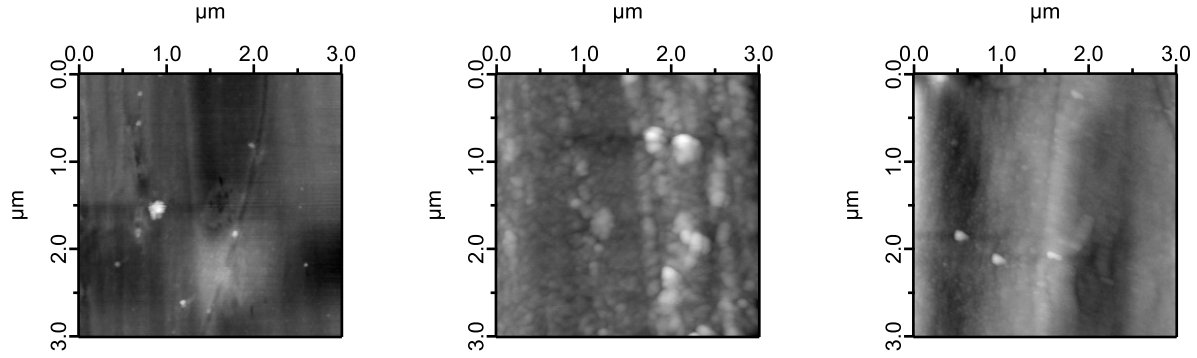
	Uncoated	PDMS	PM900	SchPFF
Fabric5	1.00	1.00	1.00	1.00
	1.01	1.01	1.00	1.01
	1.00	1.00		
Average r	1.00	1.00	1.00	1.00

Table B.5 – Roughness factors computed for the scans performed by AFM for the sample *Fabric5* and the resulting average roughness factor.

	Uncoated	PDMS	PM900	SchPFF
Fabric7	1.02	1.00	1.00	1.01
	1.01	1.01	1.00	1.00
			1.00	
Average r	1.01	1.00	1.00	1.00

Table B.6 – Roughness factors computed for the scans performed by AFM for the sample *Fabric7* and the resulting average roughness factor.

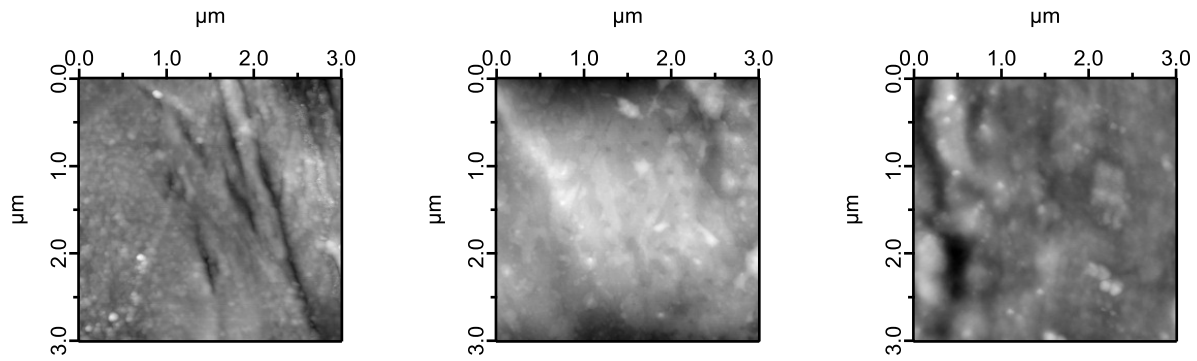
B.2 One flattened AFM scan of a single fiber for the different samples



(a) *Fabric1 without any coating. Greyscale ranges from 0 to 46 nm.*

(b) *Fabric2 without any coating. Greyscale ranges from 0 to 89 nm.*

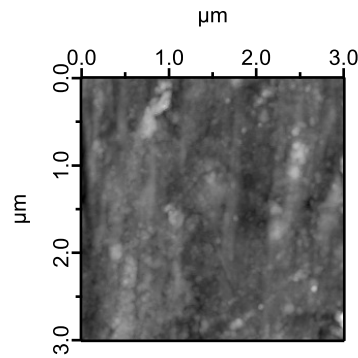
(c) *Fabric3 without any coating. Greyscale ranges from 0 to 46 nm.*



(d) *Fabric4 without any coating. Greyscale ranges from 0 to 52 nm.*

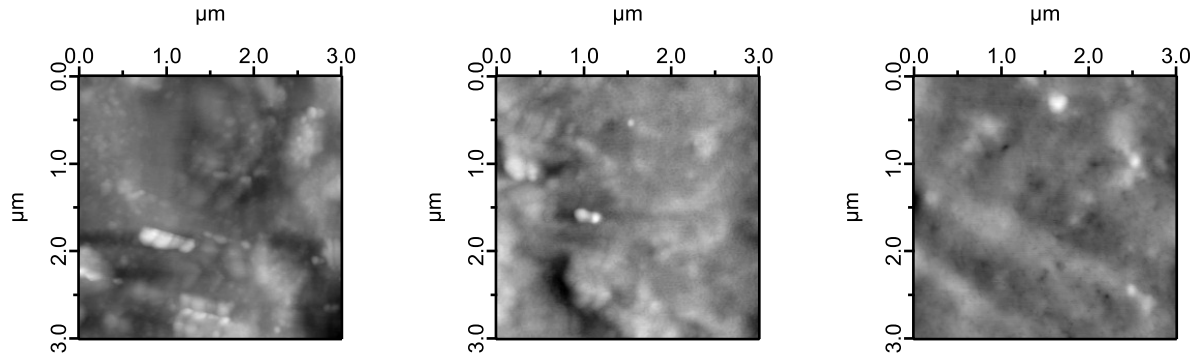
(e) *Fabric5 without any coating. Greyscale ranges from 0 to 62 nm.*

(f) *Fabric6 without any coating. Greyscale ranges from 0 to 66 nm.*



(g) *Fabric7 without any coating. Greyscale ranges from 0 to 57 nm.*

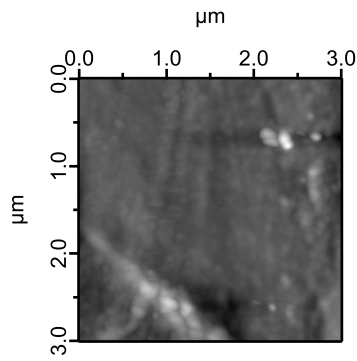
Figure B.1 – *Example of images obtained by AFM (after flattening treatment) for the different fabrics without any coating deposited on their surface. These images have a scan size of $3 \times 3 \mu\text{m}^2$ and are one of the four measurements done for each of sample.*



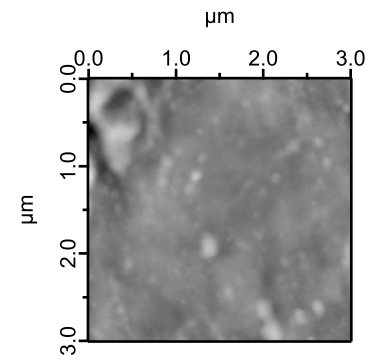
(a) *Fabric1 coated with PDMS. Greyscale ranges from 0 to 92 nm.*

(b) *Fabric2 coated with PDMS. Greyscale ranges from 0 to 89 nm.*

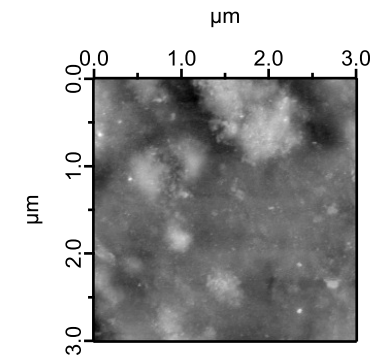
(c) *Fabric3 coated with PDMS. Greyscale ranges from 0 to 62 nm.*



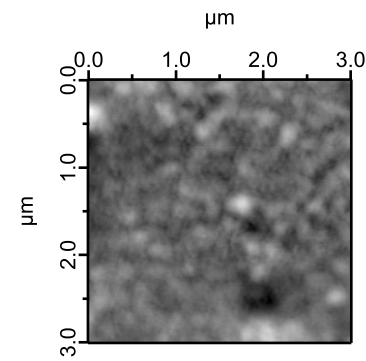
(d) *Fabric4 coated with PDMS. Greyscale ranges from 0 to 91 nm.*



(e) *Fabric5 coated with PDMS. Greyscale ranges from 0 to 79 nm.*



(f) *Fabric6 coated with PDMS. Greyscale ranges from 0 to 57 nm.*



(g) *Fabric7 coated with PDMS. Greyscale ranges from 0 to 45 nm.*

Figure B.2 – *Example of images obtained by AFM (after flattening treatment) for the different fabrics coated with PDMS. These images have a scan size of $3 \times 3 \mu\text{m}^2$ and are one of the four measurements done for each of sample.*

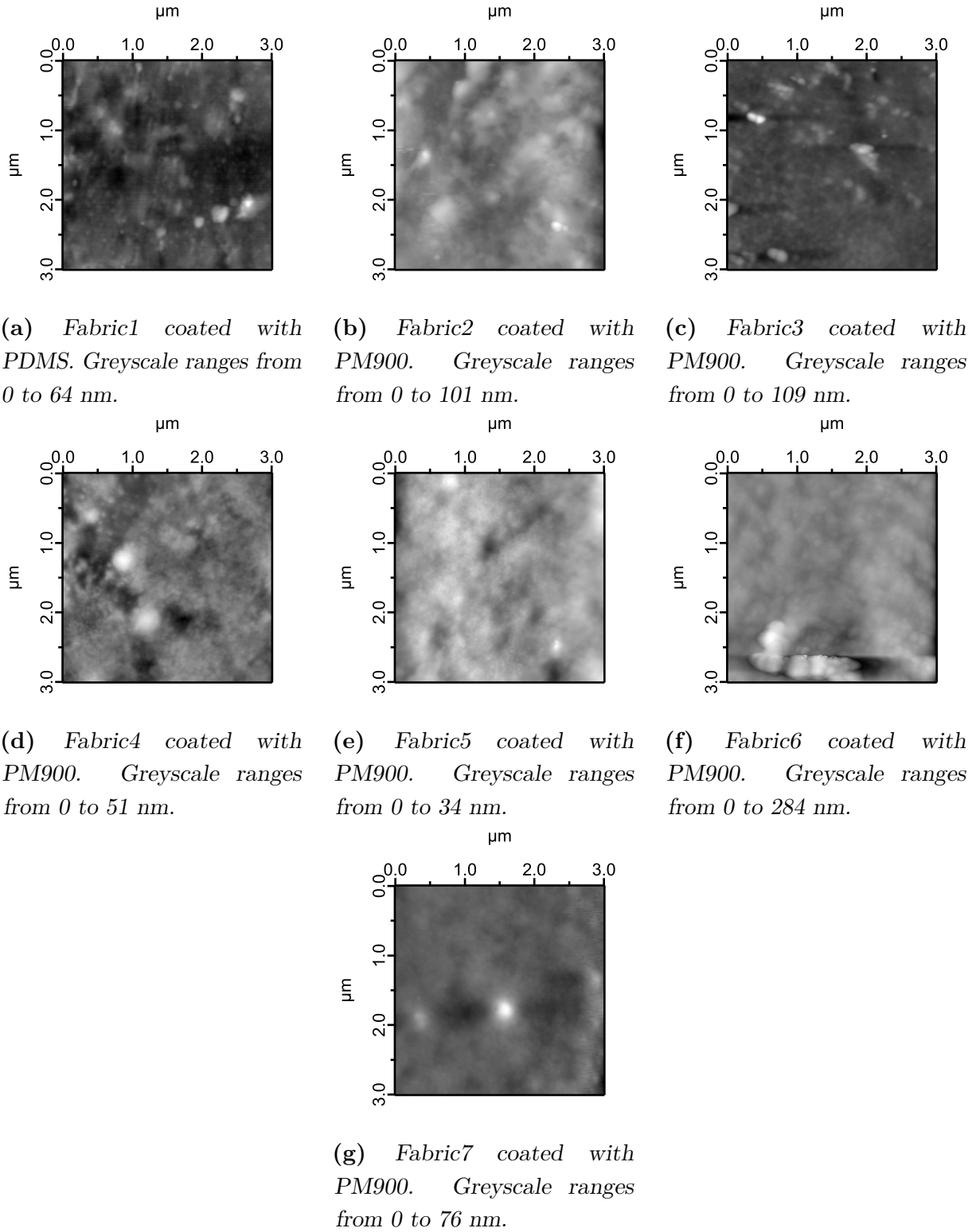


Figure B.3 – Example of images obtained by AFM (after flattening treatment) for the different fabrics coated with PM900. These images have a scan size of $3 \times 3 \mu\text{m}^2$ and are one of the four measurements done for each of sample.

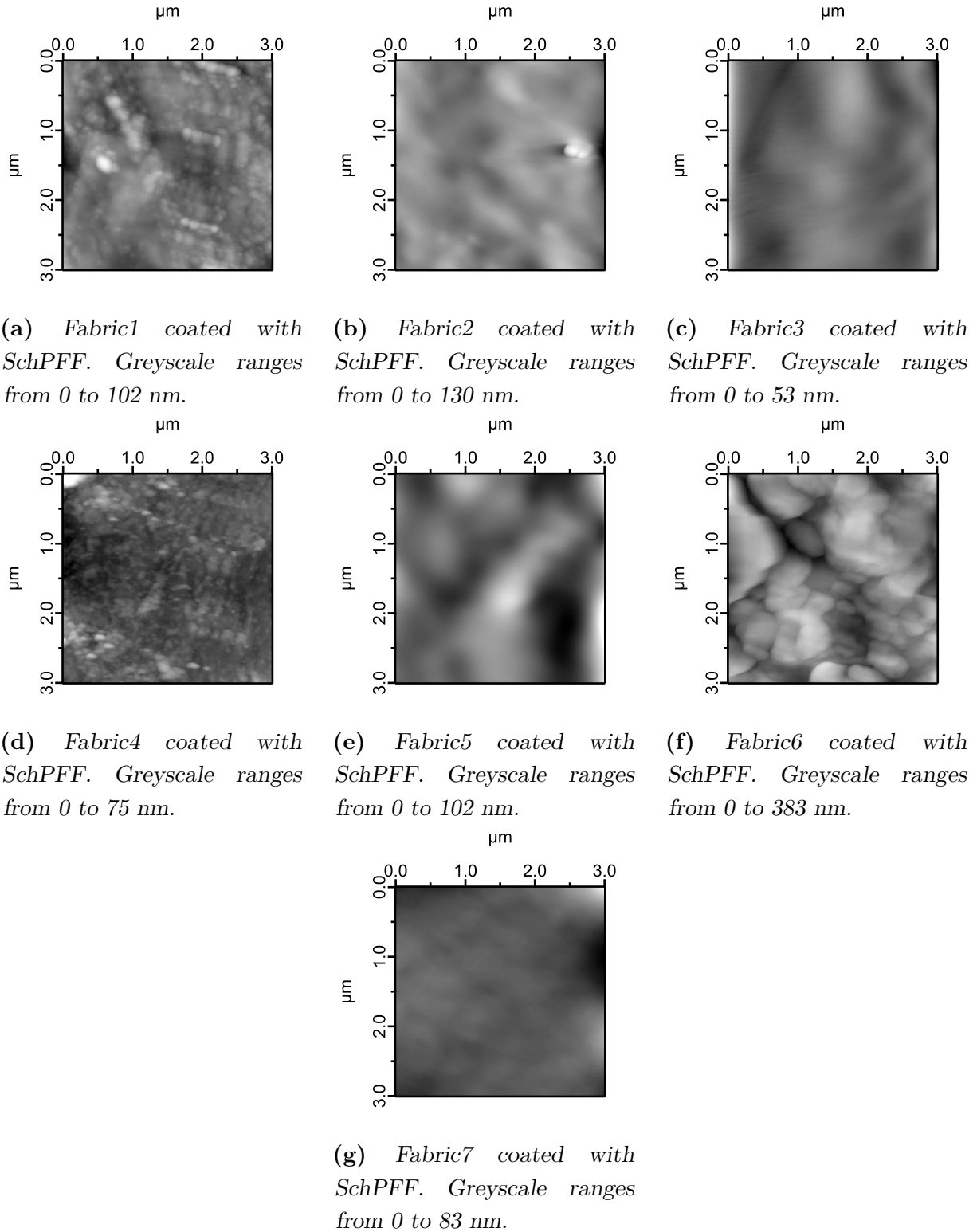


Figure B.4 – Example of images obtained by AFM (after flattening treatment) for the different fabrics coated with SchPFF. These images have a scan size of $3 \times 3 \mu\text{m}^2$ and are one of the four measurements done for each of sample.

Appendix C

Detailed data of the contact angle measurements

C.1 Measurements for fabrics coated with PDMS

Fabric1 - PDMS		
Contact angle	Left	Right
	133,9	133,5
	134,6	134,7
	129,7	129,8
	126,8	126,9
	130,7	131
	131,6	131,2
Average	131,216667	131,183333
Total Average	131,2	
Standard deviation	2,678194779	
Standard error	0,773128238	

Static roll-off angle	N/A
	N/A
	N/A
	N/A
	N/A
	N/A
Average	N/A
Standard deviation	N/A
Standard error	N/A

Dynamic roll-off angle	N/A
	N/A
	N/A
Conclusion	N/A

Fabric2 - PDMS		
Contact angle	Left	Right
	133	132,7
	131	130,7
	130,2	130,1
	129,6	129,9
	131	131,3
	130,4	130,5
Average	130,866667	130,866667
Total Average	130,866667	
Standard deviation	1,048230833	
Standard error	0,302598177	

Static roll-off angle	N/A
	N/A
	N/A
Average	N/A
Standard deviation	N/A
Standard error	N/A

Dynamic roll-off angle	N/A
	N/A
	N/A
Conclusion	N/A

Fabric3 - PDMS		
Contact angle	Left	Right
	139	138,9
	138,4	138,5
	138,4	138,4
	139,1	139,1
	139,7	140
	138,3	138,4
Average	138,816667	138,883333
Total Average	138,85	
Standard deviation	0,55840682	
Standard error	0,16119817	

Static roll-off angle	38
	45
	43
Average	42
Standard deviation	3,60555128
Standard error	2,081666

Dynamic roll-off angle	20: no roll-off
	30: roll-off
	25: little roll-off
Conclusion	20 to 30

APPENDIX C. DETAILED DATA OF THE CONTACT ANGLE MEASUREMENTS

Fabric4 - PDMS		
Contact angle	Left	Right
	135	135,8
	137,1	137,8
	137,7	137,5
	135,8	136,8
	135,9	136,3
Average	136,30	136,84
Total Average	136,57	
Standard deviation	0,9522488	
Standard error	0,30112751	

Static roll-off angle	N/A
	N/A
	N/A
	N/A
	N/A
	N/A
Average	N/A
Standard deviation	N/A
Standard error	N/A

Dynamic roll-off angle	50: small roll-off (two times)
	60: roll-off
	55: roll-off (two times)
Conclusion	50 to 55

APPENDIX C. DETAILED DATA OF THE CONTACT ANGLE MEASUREMENTS

Fabric5 - PDMS		
Contact angle	Left	Right
	138,6	138,7
	137,8	137,9
	141,6	141,4
	140,5	140,7
	138	138,2
	138	138
	139,7	139,7
Average	139,1714286	139,2285714
Total average	139,2	
Standard deviation	1,37617083	
Standard error	0,367797125	

Static roll-off angle	45
	37
	41
Moyenne	41
Standard deviation	4
Standard error	2,309401077

Dynamic roll-off angle	15 to 20
	20 to 25
	20 to 25
Conclusion	20 to 25

Fabric6 - PDMS		
Contact angle	Left	Right
	140,7	140,7
	139,2	139,3
	139,7	139,8
	139,9	140,1
	139,7	139,9
	140,3	140,3
Average	139,916667	140,016667
Total Average	139,9666667	
Standard deviation	0,47926712	
Standard error	0,1383525	

Static roll-off angle	25
	24
	37
	43
	28
	40
Average	29,66666667
Standard deviation	8,18331636
Standard error	3,65969033

Dynamic roll-off angle	5 to 10
	5 to 12
	5 to 10
Conclusion	5 to 12

Fabric7 face A - PDMS		
Contact angle	Left	Right
	137,4	137,3
	138	138
	137,5	137,8
	135	135,4
	136,4	136,55
Average	136,86	137,01
Total Average	136,935	
Standard deviation	1,06563752	
Standard error	0,33698417	

Static roll-off angle	35
	32
	32
	35
Average	33,5
Standard deviation	1,73205081
Standard error	0,8660254

Dynamic roll-off angle	20: no roll-off
	30: roll-off
	25: roll-off
	25: roll-off
	20: no roll-off
Conclusion	20 to 25

Fabric7 face B - PDMS		
Contact angle	Left	Right
	139,2	139,1
	139,2	139,2
	138,7	138,7
	139,8	139,7
	138,6	138,7
	142,7	143
	138,4	138,6
Average	139,514286	139,571429
Total Average	139,5428571	
Standard deviation	1,46167148	
Standard error	0,39064814	

Static roll-off angle	33
	34
	29
Average	32
Standard deviation	2,64575131
Standard error	1,52752523

Dynamic roll-off angle	12 to 23
	12 to 18
	13 to 20
Conclusion	12 to 20

C.2 Measurements for fabrics coated with PM900

Fabric1 - PM900		
Contact angle	Left	Right
	123,9	124,4
	124,2	123,9
	129,6	129,4
	127,8	127,9
	127,5	127,7
Average	126,6	126,66
Total Average	126,63	
Standard deviation	2,289128898	
Standard error	0,723886118	

Static roll-off angle	N/A
	N/A
	N/A
	N/A
	N/A
Average	N/A
Standard deviation	N/A
Standard error	N/A

Dynamic roll-off angle	70: no roll-off
	80: no roll-off
	80: no roll-off
	80: no roll-off
Conclusion	N/A

Fabric2 - PM900		
Contact angle	Left	Right
	131,3	131,9
	131,9	132,3
	131,8	131,8
	131,8	131,3
	131,5	131,5
	128,3	128,4
Average	131,1	131,2
Total Average	131,15	
Standard deviation	1,33790882	
Standard error	0,38622101	

Static roll-off angle	N/A
	N/A
	N/A
	N/A
	N/A
Average	N/A
Standard deviation	N/A
Standard error	N/A

Dynamic roll-off angle	30 No roll-off
	40: no roll-off
	45: no roll-off
	50: no roll-off
	60: no roll-off
	80: no roll-off
Conclusion	N/A

Fabric3 - PM900		
Contact angle	Left	Right
	138,7	138,8
	137,1	137,5
	136,5	136,3
	136	136,3
	138,1	138
	136,5	136,5
Average	137,15	137,23
Total Average	137,1916667	
Standard deviation	0,99494937	
Standard error	0,28721714	

Static roll-off angle	N/A
	N/A
	N/A
	N/A
Average	N/A
Standard deviation	N/A
Standard error	N/A

Dynamic roll-off angle	50: roll-off
	20: no roll-off
	30: roll-off
	25: no roll-off
Conclusion	25 to 30

Fabric4 - PM900		
Contact angle	Left	Right
	136,8	136,8
	138,4	138,6
	136,2	136,2
	138,4	138,3
	136,7	136,4
Average	137,3	137,26
Total Average	137,28	
Standard deviation	1,01083024	
Standard error	0,31965259	

Static roll-off angle	N/A
	N/A
	N/A
	N/A
	N/A
Average	N/A
Standard deviation	N/A
Standard error	N/A

Dynamic roll-off angle	70: roll-off
	30: no roll-off
	50: roll-off
	40: roll-off (two times)
	35: no roll-off (two times)
Conclusion	35 to 40

Fabric5 - PM900		
Contact angle	Left	Right
	137,6	137,8
	141,2	141,3
	138,4	138,5
	138,7	138,4
	140,4	140,6
	138,7	139,2
Average	139,1667	139,3
Total Average	139,2333333	
Standard deviation	1,299883445	
Standard error	0,375244028	

Static roll-off angle	N/A
	N/A
	N/A
	N/A
Average	N/A
Standard deviation	N/A
Standard error	N/A

Dynamic roll-off angle	20: no roll-off
	20: little roll-off
	25: roll-off
	30: roll-off
Conclusion	20 to 30

Fabric6 - PM900		
Contact angle	Left	Right
	142,7	142,6
	140,5	140,5
	140,2	140,7
	140,7	140,8
	139,3	139,8
	139,3	139,8
Average	140,45	140,7
Total Average	140,575	
Standard deviation	1,09969004	
Standard error	0,31745317	

Static roll-off angle	61
	41
	41
	52
	60
Average	51
Standard deviation	9,77241014
Standard error	4,37035468

Dynamic roll-off angle	20: roll-off
	10: roll-off
	5: no roll-off
	8: little roll-off
Conclusion	5 to 10

APPENDIX C. DETAILED DATA OF THE CONTACT ANGLE MEASUREMENTS

Fabric7 face A - PM900		
Contact angle	Left	Right
	140	140,1
	138,7	138,7
	139,5	139,4
	139,8	139,9
	138	137,8
	137,6	137,5
Average	138,93	138,9
Total Average	138,916667	
Standard deviation	0,99163165	
Standard error	0,2862594	

Static roll-off angle	N/A
	N/A
	N/A
	N/A
	N/A
Average	N/A
Standard deviation	N/A
Standard error	N/A

Dynamic roll-off angle	70: roll-off
	50: roll-off
	30: roll-off
	15: no roll-off
	25: roll-off
	18: no roll-off
	22: roll-off (two times)
Conclusion	18 to 22

Fabric7 face B - PM900		
Contact angle	Left	Right
	138,9	138,7
	138,7	138,7
	137,1	137,9
	138,7	139,2
	136,6	136,6
	137,6	137,6
Average	137,93	138,12
Total Average	138,025	
Standard deviation	0,91763035	
Standard error	0,26489706	

Static roll-off angle	65
	N/A
	N/A
	N/A
	85
Average	N/A
Standard deviation	N/A
Standard error	N/A

Dynamic roll-off angle	60: roll-off
	40: roll-off
	20: roll-off
	10: no roll-off
	15: no roll-off
	18: roll-off
Conclusion	15 to 20

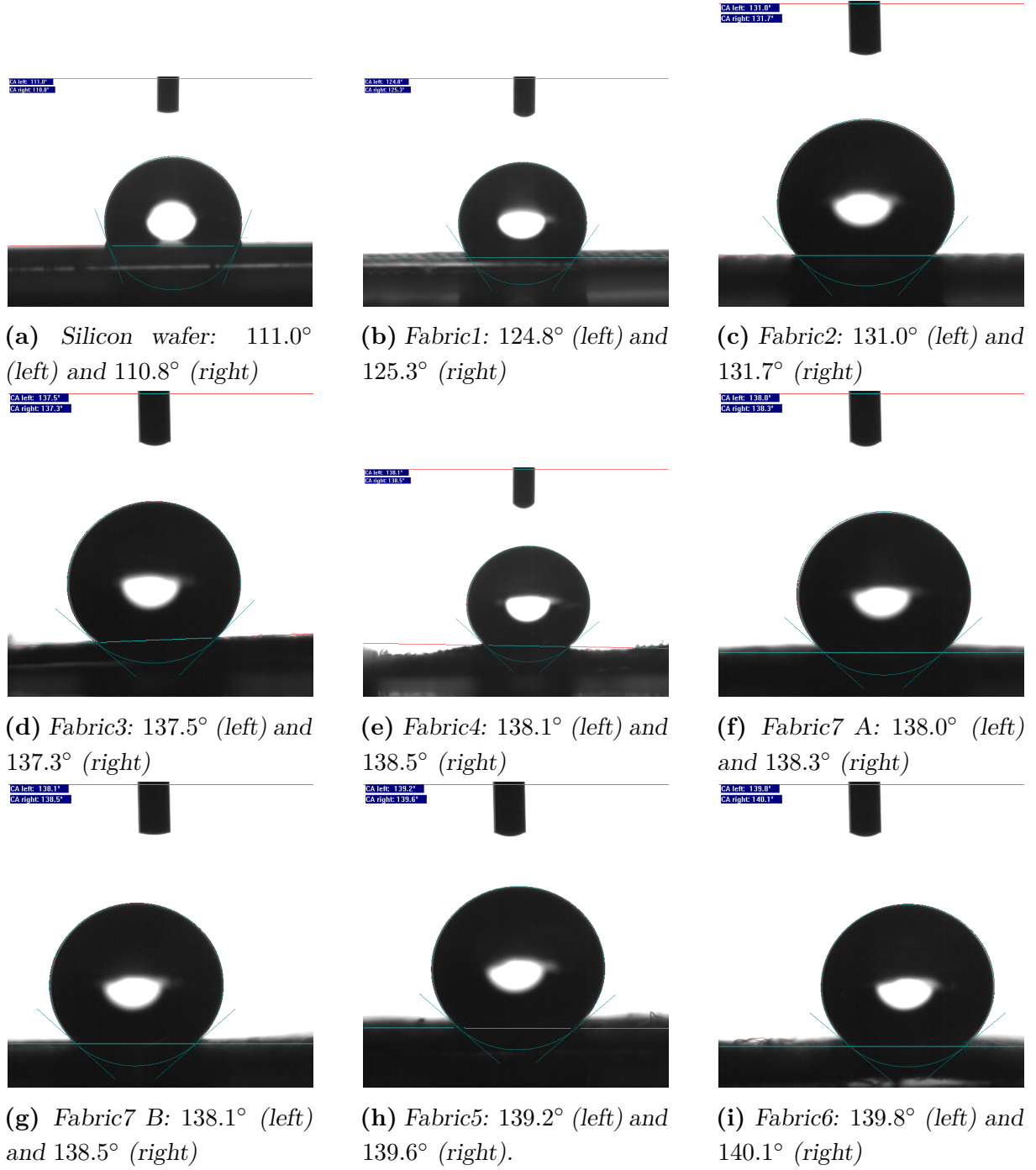


Figure C.1 – Examples of static contact angle measurements. The samples presented here are all coated with PM900. The left and right measured contact angles are given in their respective caption.

C.3 Measurements for fabrics coated with SchPFF

Fabric1 - SchPFF		
Contact angle	Left	Right
	130,5	130,4
	132,3	132,5
	130,7	130,3
	131,9	132
	133,6	133,4
	129,3	128,9
Average	131,38	131,25
Total Average	131,3166667	
Standard deviation	1,524248449	
Standard error	0,440012626	

Static roll-off angle	N/A
	N/A
	N/A
	N/A
Average	N/A
Standard deviation	N/A
Standard error	N/A

Dynamic roll-off angle	70: roll-off
	50: small roll-off
	50: no roll-off
	55: roll-off
	55: roll-off
Conclusion	50 to 55

Fabric2 - SchPFF		
Contact angle	Left	Right
	131,5	131,1
	132,5	132,4
	128,9	130
	128,2	128,6
	130,3	130
	129	129,1
Average	130,1	130,2
Total Average	130,133333	
Standard deviation	1,46370224	
Standard error	0,42253444	

Static roll-off angle	71
	69
	62
	62
	55
Average	63.8
Standard deviation	6,37965516
Standard error	2,85306852

Dynamic roll-off angle	20: no roll-off
	30: no roll-off
	40: small roll-off
	45: roll-off
Conclusion	40 to 50

Fabric3 - SchPFF		
Contact angle	Left	Right
	138,2	138,1
	137,9	138,2
	137,4	137,5
	136,6	136,9
	135,8	136
	138,5	139,1
	138,5	138,4
Average	137,557143	137,742857
Total Average	137,65	
Standard deviation	0,99518069	
Standard error	0,26597323	

Static roll-off angle	30
	24
	23
	40
	27
Average	28,8
Standard deviation	6,83373983
Standard error	3,05614136

Dynamic roll-off angle	10: no roll-off
	15: roll-off / no roll-off
	20: roll-off
	17: no roll-off
Conclusion	15 to 20

Fabric4 - SchPFF		
Contact angle	Left	Right
	137,3	136,7
	136,6	137,1
	134,3	134,9
	136,5	137,2
	136,8	136,3
Average	136,3	136,44
Total Average	136,37	
Standard deviation	0,99448479	
Standard error	0,3144837	

Static roll-off angle	40
	33
	38
	40
	29
Average	36
Standard deviation	4,84767986
Standard error	2,16794834

Dynamic roll-off angle	20: small roll-off
	25: no roll-off
	30: roll-off (two times)
	25: roll-off
	20: no roll-off
Conclusion	20 to 30

Fabric5 - SchPFF		
Contact angle	Left	Right
	138,5	138,3
	139,4	139,2
	140	140,2
	141,8	141,2
	139,9	139,9
	139,2	138,9
Average	139,8	139,62
Total Average	139,7083333	
Standard deviation	0,99163165	
Standard error	0,2862594	

Static roll-off angle	50
	47
	44
	44
Average	46,25
Standard deviation	2,872281323
Standard error	1,436140662

Dynamic roll-off angle	20: no roll-off
	30: roll-off
	25: small roll-off
Conclusion	25 to 30

Fabric6 - SchPFF		
Contact angle	Left	Right
	139,6	139,8
	141,6	141,8
	139,9	140
	138,2	138,7
	140,7	140,8
	140,5	140,4
Average	140,08	140,25
Total Average	140,1666667	
Standard deviation	1,0508294	
Standard error	0,30334832	

Static roll-off angle	15
	16
	21
	19
Average	17,75
Standard deviation	2,75378527
Standard error	1,37689264

Dynamic roll-off angle	10: roll-off
	5: small or no roll-off
	8: small roll-off
Conclusion	5 to 10

Fabric7 face A - SchPFF		
Contact angle	Left	Right
	141,8	141,8
	138,2	138,3
	140,2	140,3
	139,4	139,5
	138,8	138,7
	139,7	139,8
Average	139,683333	139,733333
Total Average	139,7083333	
Standard deviation	1,19046082	
Standard error	0,34365644	

Static roll-off angle	23
	22
	18
	17
Average	20
Standard deviation	2,94392029
Standard error	1,47196014

Dynamic roll-off angle	10: no roll-off (two times)
	15: roll-off (two times)
	20: roll-off
Conclusion	10 to 15

Fabric7 face B - SchPFF		
Contact angle	Left	Right
	138,5	138,6
	137,1	137,1
	135,7	135,9
	137,7	137,8
	139,8	139,6
	139,4	139,5
Average	138,033333	138,083333
Total Average	138,0583333	
Standard deviation	1,4151507	
Standard error	0,40851882	

Static roll-off angle	17
	22
	33
	19
	21
Average	22,4
Standard deviation	6,2289646
Standard error	2,78567766

Dynamic roll-off angle	15: roll-off
	10: no roll-off
	10: no roll-off
	15: roll-off
Conclusion	10 to 15

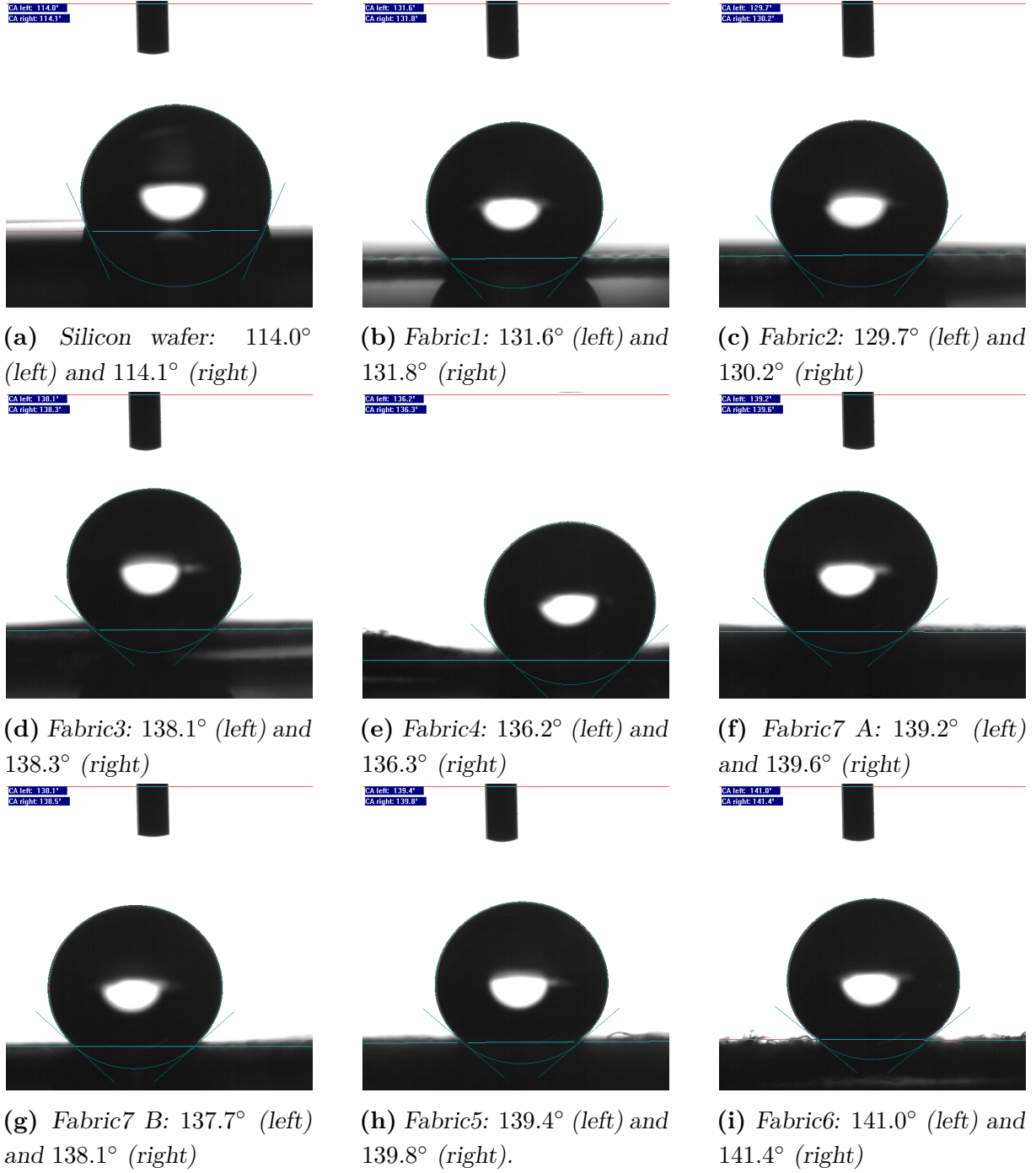


Figure C.2 – Examples of static contact angle measurements. The samples presented here are all coated with SchPFF. The left and right measured contact angles are given in their respective caption.

C.4 Measurements for the coated silicon wafers

Silicon wafer 1 - PDMS		
Contact angle	Left	Right
	116,4	116,7
	105,9	106,3
	110	110,5
	118	118,3
	108	108,5
Average	111,66	112,06
Total Average	111,86	

Silicon wafer 2 - PDMS		
Contact angle	Left	Right
	112,1	112,4
	117,7	118
	118,7	119
	108,3	108,8
	117,8	118,4
	110,2	110,8
Average	114,133333	114,566667
Total Average	114,35	

Standard deviation	4,65194648
Standard error	0,99179832

APPENDIX C. DETAILED DATA OF THE CONTACT ANGLE MEASUREMENTS

Silicon wafer 1 - PM900		
Contact angle	Left	Right
	112,5	113
	116,3	116,6
	109,6	110,2
	115,4	115,6
	115,7	116,1
	115,5	115,7
Average	114,166667	114,533333
Total Average	114,35	

Silicon wafer 2 - PM900		
Contact angle	Left	Right
	106,6	107
	108,6	108,9
	114,8	115,3
	115	115,3
	115,4	115,8
	109	109,3
Average	111,566667	111,933333
Total Average	111,75	

Standard deviation	3,36632944
Standard error	0,68714912

Silicon wafer 1 - SchPFF		
Contact angle	Left	Right
	115	115,5
	114	114,4
	114,6	115,1
	115	115,4
	114,7	115,2
	114,5	115
Average	114,633333	115,1
Total Average	114,8666667	

Silicon wafer 2 - SchPFF		
Contact angle	Left	Right
	115,2	115,5
	116,1	116,4
	115,4	115,7
	115,1	115,2
	116,2	116,5
Average	115,6	115,86
Total Average	115,73	

Standard deviation	0,64339804
Standard error	0,13717292

Appendix D

D.1 IgorPro routine written by Prof. A. Jonas to calculate the roughness factor from the scans obtained by stylus profilometry and AFM

```
// computes W(x,y) after interpolating spikes
(x-derivative larger or smaller than maxPlus or minMoins, respectively)
// stores the result in a wave ended by W_img
// assumes z in nm and x,y in um
// Used only for display
Function Transform2w(waveN,minMoins,maxPlus)
    string waveN;variable minMoins,maxPlus

    wave InW=$(waveN+"_img")
    Duplicate/O inW,$(waveN+"W_img"),X_temp2D
    wave OutW=$(waveN+"W_img")
    wave temp=X_temp2D

    variable ii,jj,kk
    variable NPx=DimSize(InW,0)
    variable NPy=DimSize(InW,1)
    Make/O/N=(NPx)/D X_temp
    Wave deriv=X_temp

    // Derivate along x
    Differentiate/DIM=0/METH=0 InW /D=temp
    temp/=1000 // convert Z-scale in um
    // and smooth along x
    ii=0
    do
        deriv=temp[p][ii]
```

```

//X_values=InW[p][ii]
jj=2    // assumes first step is OK...
do
    if ((deriv[jj] >= maxPlus) || (deriv[jj] <=
minMoins))
        // we need to interpolate
        // find next correct point
        kk=jj
        do
            kk+=1
            while (((deriv[kk] >= maxPlus) || (deriv[kk] <=
minMoins)) && (kk < NPx-1))
                if (kk == NPx)
                    // no last point found...
                    // Better to remove these points
                    deriv[jj,inf]=0
                    jj=NPx
                else
                    deriv[jj,kk-1]=deriv[jj-1]+
                    (deriv[kk]-deriv[jj-1])/(kk-jj+1)*(p-jj+1)

                    jj=kk
                endif
            endif
        while (jj < NPx-1)
        temp[][ii]=deriv[p]
        ii+=1
    while (ii < NPy)

// take the square of the derivative
OutW=temp*temp
// compute the derivatives along y - no need to smooth here?
Differentiate/DIM=1/MEIH=0 InW /D=temp
temp/=1000    // convert Z-scale in um
OutW+=temp*temp
OutW+=1
OutW=OutW^(0.5)
KillWaves /Z temp,deriv

End

```

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