

CHALMERS



Plasma Treated Water and Oil Repellent

Textiles

- Combining multi-scale surface roughness and low surface energy

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Plasma Treated Water and Oil Repellent Textiles

Combining multi-scale surface roughness and low surface energy

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Cover image: PA/PES fabric treated with a dispersion of silica particles and fluorocarbons.

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The Master Thesis project work was conducted at Swerea IVF

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Abstract

Liquid repellency is a property that is highly desirable in many textile applications. Today, liquid repellent finishes on textiles are produced by an energy demanding, three step wet chemical process that require large quantities of water and chemicals. Also, the chemicals used is often more or less toxic. Thus, more environmentally friendly and less costly alternatives are sought for.

Plasma treatment has over the last years appeared as a dry alternative to traditional wet chemical textile finishing. Plasma processing could possible increase the adhesion of an applied chemical finish by surface activation or polymerisation and cross-linking reactions. The treatment can be performed in either a vacuum chamber or at atmospheric pressure.

In this study, atmospheric plasma surface activation together with a spraying process has been employed, as an alternative to traditional wet finishing, to create water and oil repellent finishes on textiles. A spraying process consumes less water and chemicals and are more energy efficient compared to the traditional wet finishing processes.

Super repellent surfaces exhibit a low surface free energy together with a multi-scale surface roughness. Such surfaces have been found possible to create by combining low surface energy fluorocarbons and nano particles. Therefore, the aim of this study was to evaluate the combinatory effects of low energy fluorocarbons and silica particles on water and oil repellency and evaluate if the abrasion resistance could be increased by the use of plasma activation. In addition the durability of liquid repellent spray finishes was evaluated against traditional wet finishes.

Plasma activation increased the adhesion of chemicals to the textile surface. The results were most evident for fluorocarbon dispersions containing modified silica particles. However, the cross-links that are formed between the chemicals and the textile surface does not seem to be strong enough to withstand high abrasion. Spray finishes displayed high water and oil repellency exhibiting high water contact angles. However, the durability was shown to be lower compared to traditional wet chemical finishes.

Keywords textile finish, plasma treatment, hydrophobicity, oleophobicity, fluorocarbons, silica particles

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1

Introduction

FOR SEVERAL CENTURIES the textile industry exclusively consisted of fibres from natural sources like cotton, wool and silk. In the end of the nineteenth century the first 'man-made' textile fibres were synthesized and presented on the market. This become the starting point for the development of a range of synthetic polymeric fibres, the polyamides and polyesters being the first, and changed the viewpoint of textile use. Nowadays, there is a large number of available textile fibres on the market with various properties and qualities. Textiles are no longer a material limited to clothing and interior applications but a highly technical material which have opened up for a wide range of application areas [1].

The chemical and physical characteristics of the textile fibres give textile materials valuable intrinsic properties, such as flexibility, softness, low density and high strength [2]. However, the inborn properties of the textile fibres is more than often not enough to meet the high demands that are put on technical textile materials. Fire protection, tear strength, abrasion resistance, washability and water- and dirt repellency are only some of the properties wanted in today's textile materials. These additional characteristics can be achieved by various finishing processes. Traditionally, a wet chemical processing method in which the textiles are soaked in a chemical bath, padded and dried, is utilised. Since these conventional wet pre-treatments consumes large quantities of water and chemical and are extremely energy demanding, both economics and environment are affected negatively in the end [3]. Thus, there is a strong need for more environmentally friendly and less costly alternatives.

Beside the high use of resources, the chemicals used in traditional textile finishing are often more or less toxic and limiting their use is therefore highly desirable. For instance, dirt repellency is generally achieved by a treatment involving fluorocarbons (FC's). FC's exhibit extremely low surface tensions and are able to lower the surface free energy of

materials to induce high repellency towards numerous of liquids including oils. However, long chain FC's (containing eight carbons or more) have shown to be both bioaccumulating and persistent, making them harmful for both humans and the environment [4].

Plasma treatment has over the last years appeared as a dry alternative to the traditional wet textile finishing. In addition to the lower water- and chemical consumption plasma treatment only affects the outermost layer of the textile fibres. Through this surface specific modification the bulk properties of the textile fibres can be preserved. The treatment simultaneously affects the surface chemistry and the topography of the textile material and can act as an activation process in a pretreatment step or as a chemical initiator allowing for in situ polymerisations and cross-linkings. It also acts as an etchant on the surface, creating nano-structures on the material surface.

A combination of surface roughness and low surface energy are the main criterion of creating superhydrophobic and self-cleaning surfaces. Superhydrophobicity cannot only induce a water repelling character of a surface but also extend the life time of the textile material [5]. Superhydrophobicity and self-cleaning properties have been found possible to create by a combination of low surface energy fluorocarbons and nano particles to create sustainable and persistent water- and dirt repellent textiles.

Whereas traditional wet chemical approaches only relies on chemistry to achieve desired effects, the work performed in this thesis relies on the combinatory effect of surface chemistry and topography.

1.1 Aim and scope

In this master thesis project, the possibility of using a combination of traditional repellent chemicals and nano-particles is going to be examined. Plasma activation of chemically treated textiles is going to be investigated as well as the possibility of using a spraying process for distribution of chemicals. The aim of the study is to:

- evaluate the combination effect of low energy fluorocarbons and silica particles on water and oil repellency
- evaluate the abrasion resistance of plasma treated textiles as compared to un-plasma treated textiles
- optimize a spraying process for distribution of chemicals on plasma treated textiles

2

Theoretical Background

THIS CHAPTER INTEND to give an understanding of the theory that lies behind different parts of this master thesis study. The chapter starts with a general description of the textile fibres used as substrate material in the study followed by the underlying theories of hydrophobicity and oleophobicity. The concept of plasma is explained together with some different types of plasma equipments. Finally, some surface treatments to achieve repellent properties of surfaces are presented.,

2.1 Textile fibres in industry

The most commonly used textile fibres in the industry today are the polyester (PES) fibres. Polyester fibres are used in a variety of industrial applications ranging from apparel textiles to parts in medical care. Curtains for example often holds PES fibres due to their resistance towards degradation of sunlight trough the glass as they exhibit the highest UV-resistance amongst the synthetic polymer fibres.

Polyesters are semi-crystalline polymers which are produced by a condensation polymerisation in either a batch or a continuous process. The fibres are achieved by melt spinning were granules of the polymer is melted and pushed trough a spinneret. Drawing of the fibres are thereafter performed to increase the fibre strength by increasing the crystallinity.

The chemical and physical properties of textile fibres are mostly governed by the type of chemical group that joins the monomeric units in the polymer together. In polyesters that functional unit is an ester group, $-\text{COO}-$. The polarity of the ester group make polyesters fairly strong fibres. They also have high abrasion resistance and resilience. At high temperatures, polyesters can degrade in moisture by hydrolysis therefore the PES must be dried properly before melt extrusion.

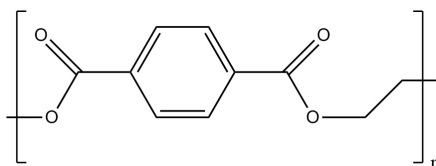


Figure 2.1: Illustration of the molecular structure of PET.

The most recognized polyester is polyethylene terephthalate (PET), which structure is presented in figure 2.1. Other polyesters include for instance polybutylene terephthalate (PBT), polyethylene naphthalate (PEN) and polycyclohexanedimethylene terephthalate (PCT) [1, 6].

The first synthetic polymer fibres to generate a serious commercial interest were the polyamides (PA). The monomeric units in PA's are held together by an amide group, $-NH-CO-$, which is responsible for most of the fibre properties. Polyamide fibres have a high resistance towards abrasion and water. They are low weight and have a good elastic recovery. Therefore PA's are often used in climbing ropes, air bags and conveyor belts. Other application areas include interior clothing, apparel and tire reinforcements.

The two most commonly used polyamides are PA6 and PA66, which structures are demonstrated in figure 2.2 [1, 7].

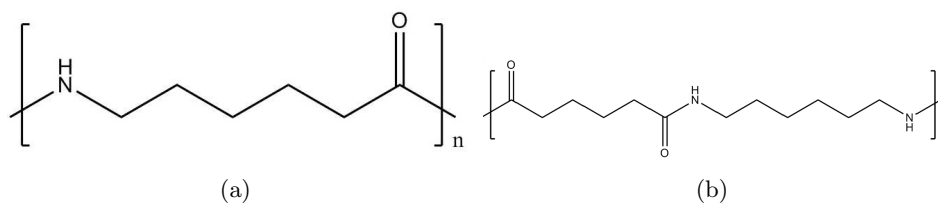


Figure 2.2: Illustration of the molecular structures of two common polyamides, PA6 2.2(a) and PA66 2.2(b).

Polyamides exist in aromatic and aliphatic forms where the latter often is referred to as 'nylons'. Just as polyesters, PA's are semi-crystalline polymers that are produced by melt spinning. Polyamides are susceptible to degradation by photo- and thermal oxidation. To prevent degradation by oxidation, the spinning process is performed in a controlled atmosphere consisting of nitrogen. Polyamides can exist in different crystal forms depending on the arrangement of amorphous and crystalline segments and the intermediate phases within the polymer fibre.

2.2 Hydrophobicity and oleophobicity

Hydrophobicity and oleophobicity refers to the ability of a surface to repel water and oil respectively. Such surface properties can be obtained by suppressing the interactions between the surface and the applied liquid substantially. By combining these inhibited interphase interactions with some degree of surface roughness a super repellent surface can be received. To comprehend the phenomenons of hydrophobicity and oleophobicity the concepts of surface tension and surface free energy must be explained.

2.2.1 Surface tension and Surface free energy

The surface repellency of any liquid is dependant on both the properties of the liquid and the solid surface and is determined by the net forces acting between the molecules in the liquid-solid interphase [1, 8]. In the bulk phase of a liquid, the interaction energies between a molecule and the surrounding molecules are equal in all directions resulting in a zero net force. At the liquid-gas interphase, however, the liquid molecules at the surface will experience a net attraction towards the molecules in the liquid bulk giving rise to the liquids surface tension, γ_{LV} . The surface tension is a measure of how strong the interaction energies are between the liquid molecules at the gas-liquid interphase. No interactions occur between the gas (vapour) phase and the liquid phase. The higher surface tension, the stronger are the forces acting between the molecules. An illustration of the forces that are acting between molecules in the liquid bulk and at the liquid-gas interphase is shown in figure 2.3.

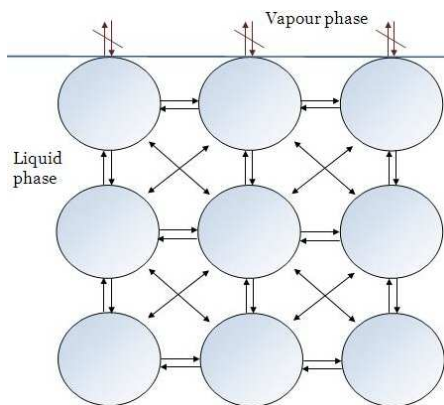


Figure 2.3: Illustration of the forces acting between water molecules in the bulk phase and at the interphase with air.

The surface free energy, γ_{SV} , can be seen as the surface tension of a solid surface and the value of it is, just as for the surface tension, dependent on the types of interactions present between the molecules at the solid surface. Strong inter- and intramolecular forces like hydrogen bonds and induced dipoles create high energy surfaces whereas weaker forces, like London dispersion forces, build up low energy surfaces [9].

When a liquid drop is placed on a solid surface a battle between the cohesive forces acting within the liquid and the adhesive forces acting between the liquid and the solid will begin. If the cohesive forces is stronger than the adhesive forces, the liquid will try to minimize its contact with the surface resulting in a balled up droplet. If instead the adhesive forces are stronger than the cohesive forces, the liquid will interact with the solid and spread across the surface. This phenomena is called wetting and is defined as the liquids ability to maintain contact with a solid surface. The degree of wetting, as illustrated in figure 2.4, can be determined by analysing the contact angle, θ , between the solid surface and the tangent of the liquid drop, see figure 2.5. A contact angle less than 90° is required for wetting to occur. Complete wetting occur when $\theta = 0^\circ$.

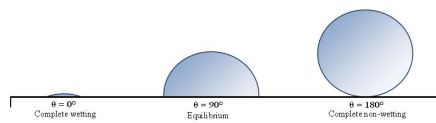


Figure 2.4: Illustration of the wetting behaviour for hydrophilic and hydrophobic surfaces.

If θ is less than 90° the surface is classified as hydrophilic if water is used and oleophilic if oil being the liquid. Contrary, if θ is higher than 90° the surface is classified as hydrophobic and oleophobic for water and oil respectively. Super repellency can be achieved at extremely high contact angles if the surface conditions are right. Super repellent surfaces are described in section 2.2.2.

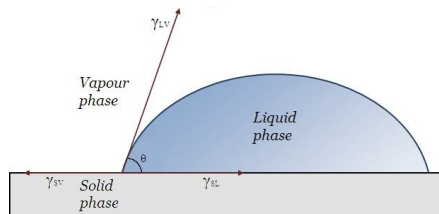


Figure 2.5: Illustration of the contact angle and interphase forces for a liquid drop placed on a surface.

For a liquid to wet a surface, the surface tension of the liquid must be lower than the surface free energy of the surface to be wet. In other words, the molecules at the solid surface must be able to interact with the molecules in the liquid. Therefore, for a surface to be hydrophobic and repel water the surface free energy of that surface must be lower than the water surface tension of 72 mN/m . Similarly, for a surface to be oleophobic and repel oil the surface free energy must be lower than $20\text{-}30 \text{ mN/m}$ which is the surface tension range of most oils [8].

2.2.2 Super repellent surfaces - surface roughness and multiple hierarchy

A surface that exhibit a contact angle greater than 150° and low roll of angle is described as super or ultra repellent. The roll of angle is defined as the tilting angle were a drop placed on a hydrophobic surface starts to roll, as illustrated below in figure 2.6. A low surface free energy is however not enough obtain the high contact angles associated with super repellent surfaces. To exhibit high liquid repellency the inhibited interphase interactions, as described in section 2.2.1, must be combined with some degree of surface roughness.

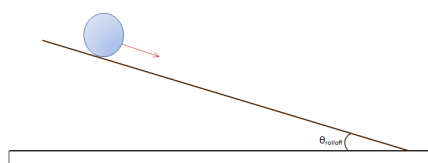


Figure 2.6: Illustration of the roll off angle, $\theta_{roll\ off}$, for a droplet placed on a tilted surface.

According to a large number of studies the best way to introduce superhydrophobicity to a surface is to mimic the structure of the lotus leaf and combine roughness in both the micrometer and nanometer size scale [15, 28, 31, 34]. The lotus leaf fulfils the criteria of superhydrophobicity by combining low surface energy wax particles in different sizes ranging from micro- to nano scales. Therefore, superhydrophobicity is some times referred to as the lotus effect. This multi-scale surface roughness effectively repel water and creates in addition minimal contact of water droplets to the surface. The hierarchical surface roughness get its effectiveness as the larger structures on the surface induce a resistance against capillarity effects, that could attract water towards the surface, in the same time as the smaller nano-structures prevent the smallest droplets from entering the cavities formed between the micro-structures [10].

Textile surfaces are naturally rough but the roughness is limited to one size scale (micrometer). To create a super-repellent surface, exhibiting high liquid contact angles and a low roll of angle, a roughness in a smaller size scales is required in addition to the larger size scale.

2.2.3 Theoretical models to describe wetting behaviour

The simplest way to describe the wetting behaviour of a liquid drop on a solid surface is given by the Young's model. The foundation of the model, which describes the relation between contact angle and surface tension, was presented by Thomas Young in a paper from 1805 [11].

$$\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} = \theta \quad (2.1)$$

In the Young's equation 2.1 γ_{SV} , γ_{SL} and γ_{LV} are surface tensions at the solid-vapour interphase, solid-liquid inter phase and liquid-vapour interphase respectively. θ is the equilibrium contact angle as described in section 2.2.1

The Young model only applies for perfectly smooth surfaces without any degree of roughness. In reality there are very few (if any) completely flat surface not least textiles. The natural roughness of a textile material enhances the surface area and influence the wetting behaviour. The first person to explain how surface roughness affect the wetting properties was Robert N. Wenzel [12]. In his paper from 1936 Wenzel described how the net force, the balance between adhesive and cohesive forces, are influenced by the increase in surface area related to roughness and introduced a roughness factor, r , as a complement to Young's equation.

$$r = \frac{\text{actual surface}}{\text{geometric surface}} \quad (2.2)$$

The geometric surface is given by the closest distance from one end to the other of a droplet on a surface (the projected area on the horizontal plane) while the actual surface corresponds to the total distance of the surface. Introducing the roughness factor into Young's equation results in the Wenzel equation 2.3:

$$\cos\theta' = r \times \cos\theta \quad (2.3)$$

where θ' is the apparent contact angle on a rough surface and θ is the equilibrium contact angle of a corresponding smooth surface according to Young's model. In the Wenzel model the liquid drop is in complete contact with the surface and enters all cavities formed between the drop and the rough surface. An extended version of the Wenzel model was presented by Cassie and Baxter in 1944 [13]. They claimed that the liquid drop and the surface produce a composite structure with air trapped in the cavities in between the drop and the surface. This adjustment make the model apply to all rough surfaces including porous structures. The Cassie-Baxter equation (2.4) is given below.

$$\cos\theta' = f_1 \times \cos\theta - f_2 \quad (2.4)$$

Just like in the Wenzel equation, θ' and θ correspond to the apparent contact angle and the 'Young's contact angle'. f_1 and f_2 represents the portion of the liquid and air in contact with the solid surface respectively. When f_2 reaches zero, and no air is trapped between the liquid and the solid, f_1 becomes the roughness factor r .

A rough surface can display both the Wenzel and Cassie states, illustrated in figure 2.7, depending on which of the two state that are the energetically more favourable.

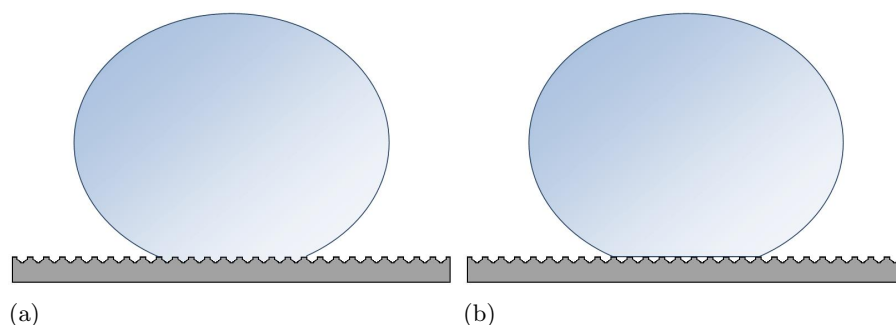


Figure 2.7: Illustration of Wenzel state, 2.7(a), and Cassie-Baxter state, 2.7(b).

Therefore the same surface can show two distinct contact angles [14]. To achieve the highest contact angles and the most hydrophobe surfaces this transition should be pushed towards the Cassie state. The composite structure with air filled cavities in the Cassie state make it easier for the liquid drop to roll of the surface opposed the Wenzel state [15].

2.3 Plasma

Plasma, often referred to as the fourth state of matter, along with gaseous, liquid and solid states, is the predominant visual matter in the universe [16]. The first person who described the plasma phenomenon was Irving Langmuir in 1929 [17]. Langmuir used the term 'Plasma' as a description of ionized gases. A plasma consists of a mixture of species with different masses and electrical charges ranging from ions, free radicals and neutrons to meta-stable excited particles and UV-radiation [1, 16, 18, 19]. A plasma is created when a gas is ionized by removing (or adding) one or several electrons from the atoms in the gas. Because of this, plasmas can exhibit different degrees of ionization varying from fully ionized to various values of partially ionized gas atoms. This results in a wide spectrum of plasma types, with unique characteristics, that make plasma useful in a large number of applications.

One interesting feature of plasma is the fact that the species in the ionized gas act together in a collective behaviour. Unlike an ideal gas, where no forces exist between the molecules, the plasma particles interact and travel together in a flowing motion. This movement of the particles can induce local concentrations of negative and positive electrical charges which produce long-distance electromagnetic fields. These Coulombic fields affect the motion of charged particles even at long distances giving rise to the characteristic collective behaviour of plasmas [16, 19].

Plasmas can broadly be divided into two categories, thermal and non-thermal plasmas, based on the relative temperatures among the constituent species (ions, neutral particles and free electrons) during treatment.

- Thermal plasmas are in thermodynamic equilibrium meaning that the electron temperature is equal to the particle and ion temperatures in the plasma. The energy density of thermal plasmas is extremely high which results in very high plasma processing temperatures.
- Non-thermal plasmas, also known as cold plasmas, exhibit lower energy density, and therefore lower working temperatures, compared to thermal plasmas. Cold plasmas are in thermodynamic non-equilibrium since the ion and particle temperature is much lower than the free electron temperature.

Due to the very high energy content, thermal plasmas can only be used to modify thermally stable inorganic materials like metals or metal oxides making them inconvenient for processing of less thermally stable materials. Cold plasmas however hold particle and ion temperatures that can go down close to room temperature making them suitable for treatment of heat sensitive surfaces like polymers and textiles [16, 19, 20].

The cold plasmas can be further divided into two groups, vacuum and atmospheric pressure plasmas, where the latter should be considered more suitable for textile production because of the possibility to incorporate it in a continuous fabrication process [21].

2.3.1 Vacuum plasma

In a vacuum plasma apparatus, the plasma state can be reached by subjecting the process gas to electromagnetic energy together with extremely low pressures. The gas molecules become partially decomposed into radicals and atoms, thus creating a plasma. The pressure needed to achieve a sufficient density of charged particles and free electrons is dependent on the electromagnetic energy frequency used. For systems operating in the radiofrequency range the working gas pressure is often retained at 0.1 mbar, whereas a source with frequencies in the microwave range operates at working pressures between 0.5 and 1 mbar. [22].

To reach such low pressures the plasma treatment is performed in a vacuum system consisting of a treatment chamber connected to a vacuum pump. This makes the vacuum plasma process fairly expensive compared to atmospheric pressure plasma procedures that are able to operate at higher pressures, see section. Further, the majority of vacuum plasma processes are only possible to utilize in batch mode. Considering the fact that most textile production processes are continuously performed, the vacuum plasma process might not be as convenient for the textile industry as the atmospheric pressure plasma system [9, 20, 22]. However, the vacuum process has its advantages as well. When working with atmospheric plasmas there is always a risk of contaminations from the surrounding air. Due to the closed working environment in vacuum processes these contaminations can be eliminated which makes the vacuum plasma process a well-controlled, reliable and reproducible technique.

2.3.2 Atmospheric pressure plasma

In atmospheric pressure plasma processes a standard atmospheric pressure is employed. The highly reactive species that constitutes the plasma is most often generated from an electrical current in an inter-electrode gap [23]. These reactive constituents have a very short lifetime due to the, for plasma physics, relative high pressure. The lifetime of the reactive plasma species can however be prolonged if the discharge are produced in a gas, for example nitrogen, that are able to affect the lifetime of the active plasma species [24].

Atmospheric pressure plasma systems are open to the surrounding environment which limits the number of substances possible to use for reaction due to health and environmental issues. Also, as already stated, the open working environment can contaminate the treated samples. On the other hand, since no vacuum pump is needed in atmospheric pressure plasma discharges both operating costs and investment cost is reduced. The lower energy consumption, together with the ability of in-line production, are the main advantages of the atmospheric pressure plasma technology compared to the corresponding vacuum plasmas [2].

For the textile industry three different discharge sources are mainly used to produce plasmas at atmospheric pressure. These are corona discharges, atmospheric pressure glow discharges and dielectric barrier discharges (DBD's) [20]. Coronas are applied in industry, but they are limited in the choice of process gas (air) and to specific substrate shape and sizes. The DBD is the atmospheric pressure plasma technique used in this thesis project and will be discussed further in the next section.

2.3.2.1 Dielectric Barrier Discharge (DBD)

The Dielectric Barrier Discharge (DBD) plasma is build up by two opposed, parallel electrodes between which the plasma field is created when applying a high voltage. One or both the electrodes are covered by a dielectric material, usually ceramic or glass, which suppresses the current and forces the discharge to propagate over the whole electrode area. This creates a uniform and non-thermal plasma suitable for processing of sensitive materials like textiles.

The distance between the electrodes is small, often a few millimetres, which together with the quite large electrode area gives to a large surface-to-volume ratio. Since the charge transport is limited by the dielectric layer the gas temperature is kept low and enables a large part of the free electron energy to excite atoms from the surrounding background atmosphere making it possible to initiate different chemical reactions.

The parallel plate set-up of the DBD makes it highly useful in continuous production settings, especially in textile finishing where the fabrics often are processed from roll to roll. Optimising of process parameters are essential to create an even treatment of the surface. Parameters that can be varied includes power density, residence time, electrode

distance and selection of process gases and carrier gas [1, 20].

2.4 Surface treatments to achieve water and oil repellent textiles

As already mentioned, the criterion of imparting water or oil repellency is to reduce the surface free energy of the surface to values below the critical surface tension of the liquid to be repelled. There are three main groups of chemicals used to modify textile surfaces to achieve water and oil repellency. These are hydrocarbons, silicones and fluorocarbons[9, 25]. All of these contain low surface energy functional groups that can reduce the surface free energy of the treated surface.

2.4.1 Repellent chemical agents

The first chemicals that was introduced as water repelling agents on the textile market were waxes. The wax was melted and padded as an emulsion onto the textile surface giving a cheap and effective repelling finish. However, the treatment was sensitive to washing and offered a low permeability of air which made more durable and comfortable alternatives more desirable.

Hydrophobic textiles based on silicones gained a lot of interest during the 1970's and 1990's due to their effectiveness even at low silicone concentrations. Silicones provide excellent protection against high energy liquids like water. However, silicones cannot reduce the surface free energy to values below 20-30 mN/m which is needed to achieve an oil repellent textile. Instead, they actually tend to attract dirt. To obtain an oleophobic surface fluorocarbons (FC's) must be utilized to some extent.

Fluorocarbons have the lowest known surface tension and are to date the only known group of chemicals that have the potential to lower the surface free energy to the low values needed to repel oil and soil. Fluorocarbons with 8 carbons (C8) or more in the chain have proven to be especially efficient for water- and oil repellency [1, 25]. However, these have also been shown to be toxic, bioaccumulating and persistent. Therefore, restrictions through laws and regulations towards the use of long chain fluorocarbons are increasing. Options are thereby sought after where the short chain (C6) FC's are the most investigated alternative to the longer C8 fluorocarbons [26].

2.4.2 Ways to apply chemicals on textiles

The most commonly used way to apply finishing agents, such as FC's, onto fabrics is by a dip process, for example the foulard process. In the first step of the process the fabric is submerged in a chemical containing bath. The wet fabric is thereafter squeezed between two rollers to remove redundant chemicals and to obtain a certain chemical pick-up before entering a final drying and curing step. The pick-up of chemicals is defined as

amount of chemicals absorbed on the fabric, as explained by equation 2.5 .

$$\text{Pick - up } \% = \frac{\text{Rolled weight of fabric} - \text{Dry weight of fabric}}{\text{Dry weight of fabric}} \quad (2.5)$$

The dip process effectively distributes the chemicals over the fabric surface resulting in high levels of liquid repellency. Also, large quantities can be processed at a high throughput. However, the technique consumes large quantities of water and chemicals and require a high energy input to evaporate remaining solvent in the drying step. This makes the dip process a fairly expensive technique with a high environmental impact.

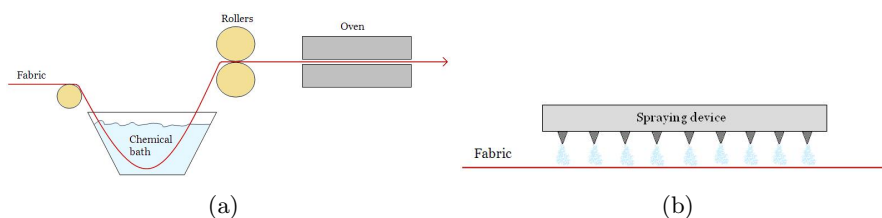


Figure 2.8: Two ways to achieve a chemical finish on textiles

An alternative way of creating a chemical finish on a textile surface is by distributing chemicals by spraying. This process is less energy demanding and consumes less water and chemicals which minimises the require to destruct left over chemicals. Spraying is therefore a more economical and environmentally friendly process compared to the conventional finishing method. Issue with a spraying process is the durability of treated material together with the uncertainties in chemical cover and chemical loss to the environment which could potentially have a negative health effect. [25].

2.4.3 Plasma modification of textile surfaces

Modifications of textile surfaces with plasma started in the 1980's [1] and there have been a lot of research in the area since. Depending on the process parameters and the chemical structure of the textile fibre to be treated, different changes can be introduced to the surface. These changes are a result of addition of removal of molecular species on the outermost layer of the substrate. There are mainly four ways to modify a textile surface by plasma treatment namely cleaning or etching, activation, grafting and polymerisation.

To achieve a cleaning or etching function with the plasma a non-polymerising gas must be employed, most commonly inert gases like argon or helium. The phenomenon is caused by detachment of low molecular weight structures on the surface. The reactive plasma species initially interacts with the textile surface by abstracting hydrogen from

the substrate, producing free radicals. Further processing leads to breakdowns of covalent bonds which in turn causes detachment of low molecular weight structures. In this manner a highly 'clean' surface can be produced. The etching effect can also be used to induce nano scaled surface structures on a smooth surface.

When a more reactive process gas is used to create the plasma discharge activation of the surface take place. Gases used for activation purposes are often oxygen or nitrogen since these are capable to induce new functional groups onto the surface. Active sites, mainly polarised groups (-OH, -COOH or $-N_2$ to name a few), are produced on the surface. These active sites increase the affinity of the treated surface to chemicals or other surfaces that easily can be anchored through chemical reactions.

Grafting, also known as functionalisation, imply that radicals that are formed in the plasma are directly deposited onto the textile substrate. This creates a permanent grafted functional group on the surface that does not detach over time. Plasma polymerisation is a process that involve a polymerisation step. An inert process gas together with monomers are utilized. The inert gas creates radicals on the surface that are able to initiate a polymerisation reaction of the monomers and in that way a polymeric layer is formed directly on the textile surface [1, 2, 27].

Plasma surface modification is still rather uncommon in the textile industry which mostly relies on wet chemical finishes. The very concept of surface modification is therefore quite new and revolutionary in the textile business. Lately, the interest of plasma modification has started to grow with the legislative and regulatory demands that are rapidly increasing regarding textile finishing chemicals. In addition, the strive towards more environmentally friendly processes is becoming more important in today's textile processes.

2.4.4 Alternatives to fluorocarbons

To date, there are no known products that can compete with the fluorocarbons in creating low energy surfaces. With their extremely low surface tension they are the only group of chemicals that can reduce the free energy of a surface to implement an oleophobic character. Extensive research has been done in the hope of being the first to present an alternative to the persistent fluorine-molecules. Many have been successful in creating superhydrophobic surfaces able to repel water with or without a self-cleaning effect[4, 28, 29, 30] but non have reported oleophobicity without some addition of fluorine-containing molecules. Right now the main challenge is to reduce the amount of fluorocarbons used in products to lower both the cost and the environmental impact. The most common option to the harmful long chain FC's are FC's that exhibit shorter FC chains. To date, no evaluations of the short chain FC's have been showing the persistent, toxic and bio-accumulating properties associated with traditionally used long chain FC's.

3

Materials and Methods

THIS CHAPTER PRESENT the methods used in this master thesis project. The fabrics and chemicals used is presented before an outline of the preparation of dispersions. Further, the equipment, parameters and settings for characterisation methods used is defined.

3.1 Materials

Two fabrics were used for treatments and analyses in this project; one pure polyamide (PA) fabric and one polyamide-polyester (PA/PES) fabric. These fabrics were treated with chemical dispersions with or without plasma treatment and compared to a laminated reference fabric made of PA. All fabrics were provided by FOV Fabrics in Borås.

3.2 Chemicals

Two different fluorocarbon dispersions (FC1 and FC2) were used to decrease the surface free energy. Three types of silica particles with different functional groups were used to enhance the surface roughness of the fabrics. The different types of silica particles and sizes are shown in table 3.1.

Table 3.1: Sizes and functional groups of silica particles used in then study.

Name in report	Particle size [nm]	Functional group
Un-modified Si	15	none
Un-modified Si	100	none
Hydrophobic Si	15	hydrophobic
Reactive Si	7	reactive

3.3 Optimising silica concentrations

The optimal amount of particles would in theory be the concentration (weight per cent, wt %) that correspond to a one single particle layer coverage of the surface. A too high particle concentration could instead of enhancing the surface roughness probably diminished it by closing the natural structure of the textile material. In an attempt to find the optimal concentration the projected area of the particles was calculated and converted to a number of particles that would be needed to cover the surface of a $1dm^2$ piece of fabric. The projected area of a sphere is the same as the area of a circle:

$$A_{projected} = \pi \times r^2 \quad (3.1)$$

Inserting the particle radius of 7.5 nm give a projected area of:

$$A_{projected} = 176.715nm^2$$

The number of particles needed to cover the surface with a single particle layer is given by 3.2.

$$N_{particles,1layer} = \frac{Area\ of\ fabric}{Projected\ area\ of\ 1\ particle} \quad (3.2)$$

Inserting the area of the fabric ($1dm^2 = 1 \times 10^{16}nm^2$) and the projected area of one particle results in a total number of:

$$N_{particles,1layer} = 5.659 \times 10^{13} \text{ particles}$$

Hence, to achieve the optimal concentration in wt %, 5.659×10^{13} particles need to be applied onto a $1dm^2$ textile sample. The number of particles together with the volume of one particle can be used to calculate the total volume of particles needed. The volume of particles can thereafter give the weight per cent of particles. The volume of one particle is:

$$V_{particle} = \frac{4\pi r^3}{3} \quad (3.3)$$

Inserting value of particle radius result in a particle volume of:

$$V_{particle} = 1.767 \times 10^{-21} dm^3$$

Number of particles, $N_{particles}$ on $1dm^2$ fabric will together with the particle volume, $V_{particle}$ give the total volume of particles needed on $1dm^2$ fabric:

$$N_{particles} \times V_{particle} = Volume\ of\ particles\ on\ 1dm^2\ fabric = V_{tot} \quad (3.4)$$

Finally, the mass of particles, $m_{particles}$ can be calculated by using the density of silica, $\rho_{Si} = 2600 \frac{g}{dm^3}$, and the total volume of particles, V_{tot} :

$$m_{particles} = \rho_{Si} \times V_{particles} \quad (3.5)$$

Inserting numbers give the mass of particles that should be applied per $1dm^2$ fabric:

$$m_{particles} = 0.00026\ g$$

1 g of solution per dm^2 fabric would results in a silica concentration of 0.026 wt%.

In these calculations the fabric surface is approximated as a smooth. In reality the true surface area of the fabric is larger due to the roughness. Therefore, the number of particles to saturate the surface with a single particle layer should be somewhat larger. Introducing a roughness factor for the fabric might give a more likely concentration. According to measurements performed by D. Semnani et.al. [32] the average surface roughness factor, K_f , for 15 different weft knitted fabrics was 0.10928.

Dividing the mass with this roughness factors results in a concentration of 0.237 wt % Si. Three concentrations close to the calculated concentration (0.15 wt %, 0.20 wt % and 0.25 wt %) were thereby evaluated for the 15 nm sized silica particles. The same calculations were used for determining concentrations of the particles with other sizes. Based on experiments by Nimittakoolchai et. al. [31], a higher concentration of 3 wt% un-modified, 15 nm sized, silica particles was also evaluated.

For the reactive silica particles, that exhibit a smaller diameter of 7 nm, the calculated mass of particles, to create a one particle layer, were to low to accurately be able to weight in on the available scales. Instead higher concentrations of these particles was used to evaluate the effect of higher concentrations. Concentrations from 0.5 wt % to 12 wt % were examined.

3.4 Preparation of dispersions

Two preparation routes were used for processing of dispersions. The starting experiments were done by applying dispersions of silicon particles and fluorocarbons separately in a two step process. Purchased fluorocarbon dispersions of 100 wt% was diluted to concentrations of 5-100 wt% in distilled water. Preparations of silica dispersions were done by dispersing silica particles (0.2-5 wt%) in 2-isopropanol. The ready silica dispersion was stirred for 45-60 minutes before use.

To reduce the processing steps, a mixed dispersion of fluorocarbons and silica particles was tested. To start with, 100 wt% FC dispersion was diluted to a desired concentration (5-100 wt%) in distilled water. Thereafter, un-modified silica particles were weight in and added to the prepared FC dispersion to a desired concentration (0.01-5 wt%). Prepared FC-Si dispersion was stirred vividly 45-60 minutes before use.

Dispersions of reactive silica particles were prepared by diluting a silica sol (28 wt% Si) to concentrations of 0.5-12 wt%. The diluted sol were added to 5 wt% FC and stirred vividly 30 minutes before use. Samples treated with hydrophobic silica particles were prepared in a two step process as the hydrophobic particles are not compatible with distilled water. Hydrophobic silica particles were dispersed in 2-isopropanol to a concentration of 0.2 wt%. The prepared dispersion was stirred vividly 45-60 minutes before use.

3.5 Spraying process

The chemical dispersions were distributed by a spraying process were a small air brush (Biltema) was used as spraying equipment. Repeated tests were done to ensure reproducibility. Two routes for applying of dispersions were used; spraying of silica and fluorocarbon dispersions separately and spraying silica and fluorocarbon dispersions together as a mixed dispersion of the two chemicals. The first route was employed for hydrophobic silica particle dispersions and the second spraying route was used for dispersions containing reactive silica. Both spraying routes were tested for dispersions exhibiting un-modified silica particles.

Fabrics were weighed before and after spray treatment with dispersions. Approximately 1 g solution per dm^2 fabric (0.94-1.33 g/dm^2) was applied on each sample. Treated samples was dried over night and thereafter cured at 160 °C for 1 minute. The spraying pressure used was 3.5 bar and the spraying distance to the fabric was approximately 10 cm.

3.6 Plasma equipment and treatment procedure

The plasma processing was performed in a PLATEX 600 LAB dielectric barrier discharge (DBD) plasma made by GRINP, Italy. In the DBD equipment the plasma discharge is normally created between two parallel electrodes as described in theory section 2.3.2.1. In this study however, only one electrode was used. The second electrode was replaced with a grounded metal plate. Three process parameters were varied: the process gas used, the energy density (power) of the plasma and the time the fabrics were in the plasma zone. Plasma treatment was employed both as a pre-treatment and as a post-treatment i.e. both before and after applying dispersions.

Helium was used as process gas both for pre-treatments and post-treatments with plasma. When plasma processing was used as a sample pre-treatment an addition of oxygen was done resulting in a combination of helium and oxygen as process gas. The oxygen flow was set to 0.2 Litres/minute. For the post-treatments, pure helium was used to avoid a hydrophilic finish.

The energy density of the plasma discharge (treatment power, W) were varied between 160-400 W. The processing time was varied by repeating the plasma treatment 2-4 times (40-80 seconds). Other process parameters that can be varied but were kept constant are shown in table 3.2.

Table 3.2: Constant plasma processing parameters

Process parameter	Value
Distance between electrode and grounded plate	3 mm
Speed of frame	1
Electrode temperature	30°C
Gas flow of helium	5 Litre/minute

Treated samples were covered with aluminum foil directly after plasma treatment to avoid breakdown of the activated surface by ageing. Spraying of dispersions were performed within 3 hours to prevent breakdown of plasma activated sites.

3.7 Oil repellency test

The oleophobic character of the fabrics was evaluated according to the Swedish standard SS-EN ISO 14419:2010. A total of eight oils with decreasing surface tension were carefully applied onto the sample with a glass pipette. The apparent contact angle and spreading of the drop was estimated after 30 seconds and compared to pictures and descriptions.

The oleophobicity grade corresponds to the highest number of test liquid that do not wet the textile surface. The sample should be able to repel the hydrocarbon for more than 30 seconds and three of five drops must display a droplet shape to pass the test. The best oil repellency grade that can be achieved according to this standard is 8 [2]. Table 3.3 show the surface tension and density of the eight testing liquids.

Table 3.3: Specific surface tension and density for the test liquids (hydrocarbons) in the standardised oil repellency test SS-EN ISO 14419:2010

Hydrocarbon composition	Test liquid number	Surface tension [mN/m]	Density [kg/dm ³]
Paraffin oil	1	31.5	0.84-0.87
65 vol% White mineral oil + 35 vol% n-hexadecane	2	29.6	0.82
n-hexadecane	3	27.3	0.77
n-tetradecane	4	26.4	0.76
n-docecane	5	24.7	0.75
n-decane	6	23.5	0.73
n-octane	7	21.4	0.70
n-heptane	8	19.8	0.69

3.8 Spray test

The hydrophilic character of the treated samples was measured according to a standard spray test (24920:1992 SS EN, 4920:1981 ISO). Measurements was performed in a controlled climate at a temperature of 20°C and a relative humidity of 64 %. Samples at a size of 180 × 180 mm was mounted at an angle of 45° below the funnel used to stimulate a rain fall. Distillate water of a temperature of 20°C and a volume of 100 mL was poured trough the funnel, spraying the fabric samples. The sprayed samples were graded according to standards ISO 1-5 as demonstrated below.

ISO 1 - Wetting of both sides of sprayed sample surface, complete wetting

ISO 2 - Wetting of sprayed side of the fabric

ISO 3 - Partial wetting of the sprayed surface

ISO 4 - No wetting but sticking of small droplets

ISO 5 - No wetting or adherence of droplets

3.9 Contact angle and surface free energy

The contact angles and surface free energies were measured using a drop deposition method in which a drop of liquid is placed on a solid surface. Images are taken of the drop and analysed by computer software. The measurements are usually automated and computerised which enables a higher degree of reproducibility compared to manual operation [8, 33].

Measurements of the water contact angle and the surface free energy were performed using a Krüss DSA30E instrument from Krüss GmbH, Germany. For the SFE calculations two test liquids, water and diiodomethane were used. All values calculated as a mean of three test cycles (30 measurements).

3.10 Scanning electron microscopy

Scanning electron microscopy (SEM) is a technique that utilizes electrons to produce an image of a solid surface. A focused high-energy electron beam interacts with the surface atoms of the sample, creating a picture of the surface based on a variety of emitted species. SEM detects different types of electrons and is also capable to analyse x-rays produced by inelastic electron collisions. The detected electrons provide information regarding chemical composition, morphology and crystalline structure while the x-rays give indications of which elements the sample consists of. Secondary- and backscattered electrons are most commonly used to achieve an image of the sample.

There are two types of SEM apparatus based on the analysing pressure. The traditional SEM operates in high vacuum which gives superior resolution but requires sample preparation. For example the samples must be conducting, dry and compatible with vacuum. To minimize the sample preparations, a low vacuum scanning electron microscope can be used. These cannot give as high resolution but the samples do not have to be conductive. This makes it possible to analyse non-conducting materials like textiles without sputtering them with a metal [33].

The SEM analysis was performed with a 6610 LV from JEOL, Japan, microscope. Small pieces of sample were mounted on a carbon tape and placed in the SEM vacuum chamber.

3.10.1 Martindale abrasion

Martindale is a standardised testing method used for evaluation of the abrasion resistance of fabrics. Martindale abrasion tests were performed on circular samples with a diameter of 38 mm. Samples were mounted on a sample holder and rubbed against a standard wool fabric for 5000 cycles at a load of 12 kPa. The permanence of the applied coating was evaluated by measuring oil repellency, water repellency, surface free energy and water contact angles before and after the Martindale abrasion test.

4

Results and Discussion

IN THIS CHAPTER the result of analyses performed on treated fabrics in the study will be presented. A continuous discussion will be held simultaneously as the results are presented. Results achieved from analyses of the reference fabric are presented first followed by a discussion regarding the spray processing method. Further, an evaluation of suitable fluorocarbon (FC) concentrations and different types of silica (Si) particles are presented. Water contact angle (CA) and surface free energy (SFE) results together with results from water and oil repellency tests for non-plasma activated, spray treated samples are presented. Finally, the impact of plasma treatment will be evaluated and discussed.

4.1 Reference sample

The reference sample, a water and oil repellent fabric produced by FOV Fabrics (Borås) and used in industry today, was evaluated for comparative reasons. Table 4.1 show the results of oil- and water repellency tests together with values from CA and SFE measurements before and after Martindale abrasion (5000 cycles, 12 kPa).

Table 4.1: Results of oil repellency, water repellency, water contact angle and surface free energy before and after Martindale abrasion 5000 cycles. Results are valid for the reference sample treated with conventional fluorocarbon treatment.

Evaluation method	Value before abrasion	Value after abrasion
Oil repellency	6	4
Water repellency	ISO 4	ISO 3
CA	126.0	120.1
SFE	4.7	13.4

The results presented in table 4.1 show that the reference fabric exhibit a hydrophobic character both before and after abrasion. However, the abrasion has a negative impact on all evaluated parameters. A negative impact is illustrated by a decrease in CA and oil/water repellence and an increase in SFE.

The highest oil repellency grade that can be achieved in the standardised testing method is 8. A repellency grade of 4, as the reference displayed after abrasion, give a fairly good repellency and can repel liquids with surface tension above 26.4 mN/m (values displayed in table 3.3). This implies that the reference sample has a high oil repellence both before and after abrasion. In the water repellency tests, the reference fabric showed an water repellency grade of ISO 3 after abrasion. ISO 3 implicate a relatively good repellence (description of repellency grades are presented in section 3.8) which imply that the reference fabric has an acceptably good water repellency both before and after abrasion. All in all, the reference fabric displayed a hydrophobic character with good repellent properties both before and after abrasion. Although, as the fabrics in question often are used for extreme applications, like protecting clothing, there is room for improvements.

The results achieved form analyses of the reference fabric will be used as a comparison between the traditional wet finishing foulard process and the spraying method used in this project and will serve as guidelines for the discussion.

4.2 Spraying process

To ensure reproducibility, repeated spraying tests with dispersions holding constant silica concentrations were performed. The water contact angle for the repeated tests were evaluated showing a standard deviation of 6.96 for 10 treated samples. This indicates that the spraying process employed in this study gave reproducible results. Hence, the spraying method should not affect the test results when working in small scale as in this project. Fabric samples were sprayed with approximately 1 g dispersion per dm^2 fabric (0.94-1.33 g).

The primary reason for replacing traditional wet finishing processes like the foulard process with a spraying process is that spraying consumes less water and chemicals. Hence, spraying of chemicals would be beneficial both for environmental and economical reasons. However, care must be taken as to what type of chemicals that are sprayed as spraying creates very fine droplets and/or particles i.e. aerosols. These aerosols might cause hazardous affects on health, if being toxic or in other way harmful, as they easily can enter the body both trough breathing and through the skin. Effective ventilation and processing in breathing fumes is therefore important when working with spraying applications.

Uneven distribution of chemicals is another problem related to spray processing. As

previously mentioned, the repeated testings showed a relatively low deviation in water contact angle measurements for spray treated samples in this study. However, the size of these samples have all been quite small (2 dm²-22 dm²) and up scaling the process might give a larger variety in the results. Therefore, complimentary evaluations of reproducibility is needed before larger scale productions.

4.3 Choice of Fluorocarbon dispersion

The main intention of the fluorocarbon dispersions (FC's) is to induce oleophobicity to the treated fabric samples. Therefore, the first evaluations of the FC dispersions was based on the treated fabrics ability to repel oils in a standardised oil testing method. Two types of commercially available FC dispersions were evaluated at different concentrations. Evaluations of the FC dispersions were done both with and without addition of silica particles.

Fabrics treated with the first evaluated fluorocarbon dispersion (FC1) showed an oil repellency grade of 6 for the pure FC dispersion (without addition of Si-particles), which is comparable to the oil repellency grade of the reference sample as shown in table 4.1. Different concentrations of FC1 were examined with equal results for both PA and PA/PES fabrics. Unfortunately the oil repellency grade decreased to 4 when silica particles were introduced in the FC1 dispersion. The reason behind the decrease in oil repellence is difficult to explain since the complete molecular structures of the evaluated dispersions are not known. The dispersions do not only consist of fluorinated carbon chains but also other molecular structures. Therefore, there are most likely some structure in the FC1 dispersion that are not compatible with the silica particles.

In an attempt to increase the compatibility between the FC1 dispersion and the silica particles, plasma treatment (as will be discussed further in section 4.6) of the fabrics were performed. Different treatment powers and treatment times were examined as well as using plasma before and after applying the chemicals. However, instead of increasing the oil repellency grade the plasma treatment seemed to decreased it. Thereby, no further tests were done with the FC1 dispersion.

The second FC dispersion (FC2) was evaluated in the same manner as FC1. Fabrics treated with pure FC2 (without silica particles applied) demonstrated an oil repellency grade of 8 indicating the highest repellency grade in the standardised testing method. A combination of FC2 and silica particles displayed the same oil repellency grade, implying that the molecular structures in FC2 are more compatible with the silica particles as compared to FC1. Evaluations of different FC2 concentrations were performed to examine if the high repellency was concentration dependent. Concentrations ranging from 100 wt% to 5 wt% FC gave equal results in oil repellency. Thus, the repellent properties appear to be independent of the FC concentration. 5 wt% FC seems to be adequate to achieve excellent oil repellent properties of the treated fabrics. Both fabrics,

PA and PA/PES, showed the same results in the oil repellency tests. A summary of the oil repellency grades for fabrics treated with FC1 and FC2 are presented in table 4.2 together with results for the reference fabric.

Table 4.2: Results from oil repellency tests for fluorocarbon dispersions FC1 and FC2 as compared to a reference fabric. Oil repellency grades are presented for fabrics treated with FC dispersions both with and without silica particles. Results are valid for both PA and PA/PES fabrics.

FC type	Oil repellency without Si particles	Oil repellency with Si particles
FC1	6	4
FC2	8	8
Reference	6	-

Evaluations of CA's and SFE's of FC2 treated fabrics were done in addition to the oil repellency tests. The same concentrations (100 wt% to 5 wt%) as evaluated in the oil repellency tests were examined. A high oil repellence in combination with high water contact angles and low surface free energies would give the most suitable candidate. The results of the CA and SFE measurements are presented in figure 4.1.

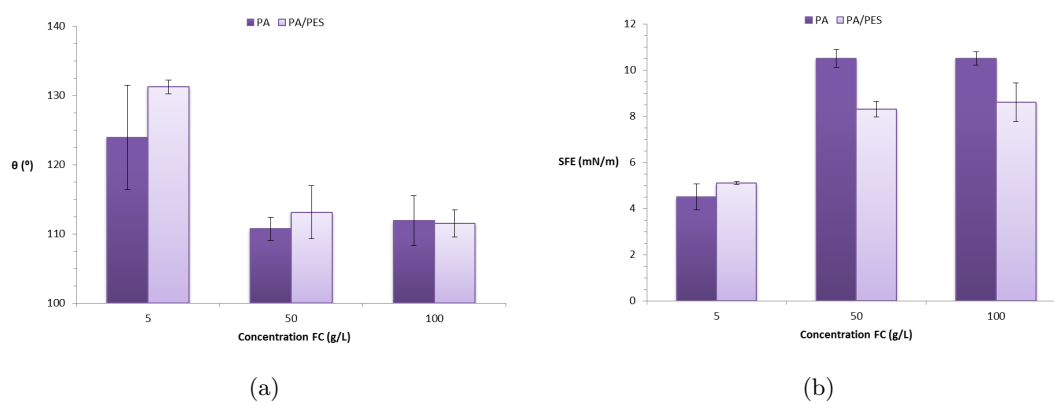


Figure 4.1: Water contact angles 4.1(a) and surface free energies 4.1(b) of fabrics treated with different concentrations of FC2 dispersion without silica particles added. Values for both PA and PA/PES fabric illustrated. CA results are based on measurements of water contact angle at 3 points of the treated sample (30 values in total) while SFE results are based on measurements at 3 points each for water and di-iodine-methane of the treated sample (60 values in total).

As can be seen in figure 4.1(a), both PA and PA/PES fabrics show similar CA's for the different FC2 concentrations. The highest CA's are displayed at the lower concentration

of 5 wt%. Fabrics treated with 50 and 100 wt% FC2 show comparable CA's that is somewhat lower than for the 5 wt% concentration. Results from surface free energy tests, shown in figure 4.1(b), demonstrates a similar effect of the FC2-concentration. Fabrics treated with 5 wt% FC2 displayed the best (lowest) SFE values. The apparent decrease in water contact angle at higher concentrations might be explained by a saturation of FC's on the fabric surface. This could reduce the natural surface roughness of the material which in turn would result in lower CA values. As the SFE is related to the CA a reduction in CA would also affect the SFE negatively and increase the SFE values.

One of the reasons for using textile materials is often the flexible character of the material. A decrease in flexibility is therefore highly unwanted. A saturation of the fabric surface could not only affect the CA's and SFE's but could also interfere with the flexibility of the treated fabrics. Fabrics treated with 5 wt % FC2 did not lose any of their flexibility but treatment with FC2 concentrations above 15 wt% resulted in an increased stiffness. Thus, a lower concentration of FC is once again beneficial. Also, from an environmental and economical point of view a lower concentration of FC is of course to strive for since fluorocarbons are relatively costly and has proven to be both toxic and persistent in nature.

The CA and SFE values for fabrics treated with 5 wt% FC2 are also comparable with values achieved for the reference fabric as demonstrated in table 4.3.

Table 4.3: CA and SFE values for PA and PA/PES fabrics spray treated with 5 wt% FC2 dispersion as compared to a traditionally used reference fabric.

Fabric	CA	SFE
PA	124.0	4.5
PA/PES	131.2	5.1
Reference	126.0	4.7

Hence, the samples were treated with a constant concentration of 5 wt% FC2 as this concentration gave the best results in CA and SFE measurements. In further results and discussions fluorocarbon dispersion 2 will be presented as FC instead of FC2.

4.4 Silica particles

In an attempt to create a surface roughness similar to the lotus leaf, silica particles were applied onto the fabric surface, together with the fluorocarbon dispersion. Combinations of two particle sizes, 15 nm and 100 nm, as well as uniform particle sizes were tested and evaluated. Several particle concentrations were examined as will be further discussed in the upcoming sections. The natural roughness of the fabric will represent the micrometer sized surface structures. An addition of smaller particles in the nanometre regime could

hopefully be sufficient to create a surface exhibiting a multi-scale roughness similar to the louts leaf.

The starting trials were performed with un-modified silica particles having an uniform particle size of 15 nm. The first tested concentration of un-modified silica particles was 3 wt%. This concentration was chosen based on the research done by Nimitrakoolchai and Supothina [31]. In their paper from 2012 they concluded that a concentration of 3.333 wt% of SiO_2 was adequate to induce ultra hydrophobicity and super oleophobicity to a glass surface. Unfortunately, when spray treating the fabrics with silica dispersions with this concentration a white precipitate could be seen on the textile surface. This indicated a saturation of white silica particles on the surface. Scanning electron microscopy (SEM) confirmed that the surface was completely covered with silica particles. Therefore, lower particle concentrations were evaluated.

It is of course crucial that the treated fabric is sufficiently resistant to wear and tear from the surrounding environment. Thus, the anchoring of silica particles to the textile fibres is of outermost importance. The anchoring of silica particles to the fabric surface is dependent on both the reactivity and compatibility between the particles and also the chemical structures that build up the textile material. Pure silica particles (un-modified silica) might form cross-links to the textile fibres, see figure 4.2, as hydroxyl groups located on the particle surface interact with active molecular structures on the fabric surface. Plasma treatment of the fabric surface could possibly increase the amount of active sites by creation of surface radicals.

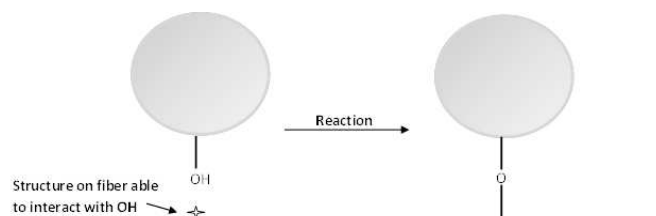


Figure 4.2: Illustration of a cross-link that might be formed between the fabric and the un-modified silica particles.

In addition to the un-modified silica particles, silica particles with a reactive functional group (reactive silica) were tried out. In theory, a reactive functional group should be more prone to create cross-links and chemical bonds to a plasma activated fabric surface. The plasma produced, reactive sites should be able to induce a reaction with the reactive functional group on the silica particles and thereby create a chemical bond between the particles and the textile fibres.

Finally, silica particles modified with a hydrophobic functional group (hydrophobic silica) were evaluated as well. A hydrophobic group should not affect the ability to react with

the molecular structures in the fabric (as it does not exhibit any reactive elements) but it might increase the water repellency and water contact angles after abrasion as the particles in them selves are more hydrophobic as compared to un-modified silica particles.

4.5 Combination of fluorocarbons and silica particles

As stated earlier, a combination of low energy fluorocarbons and silica particles would in theory present the best results in CA and SFE measurements. Part of the aim of this study was to evaluate if a combination of FC and silica particles actually display higher CA's and lower SFE's as compared to pure FC dispersions without addition of particles. The following sections present how the water and oil repellence together with the CA and SFE are affected by different concentrations and types of silica particles in FC dispersions of a constant concentration of 5 wt%.

4.5.1 Hydrophobicity and oleophobicity

For the 5 wt% FC dispersions with un-modified silica particles, the particle concentration did not have an substantial impact on the hydrophobicity of the treated textile samples. Comparable water repellency grades were achieved for all evaluated particle concentrations both before and after Martindale abrasion (5000 cycles, 12 kPa) as demonstrated in table 4.4. Water repellency grades for 15 nm sized and a mixture of 15 nm and 100 nm sized un-modified silica particles are shown in table 4.4(a) and 4.4(b) respectively. The results refer to both PA and PA/PES fabric as both fabrics displayed similar water repellency grades.

The repellency grades before abrasion, as presented in table 4.4, demonstrates that fabrics treated with a dispersion of un-modified silica particles and 5 wt% FC have a high repellency towards water. ISO 5 is the highest repellency grade that can be achieved and express a complete repellency of water. ISO 4 imply no wetting of the surface but with some sticking of small droplets. However, after abrasion the water repellent character of the fabrics was completely (ISO 1, total wetting) or almost completely (ISO 2, wetting of sprayed side) lost. The decrease in the water repellency after abrasion is most likely due to loss of silica particles and FC's. The cross-links that could form between the particles and the textile fibres, as illustrated in figure 4.2, are most likely not strong enough to withstand the impact from the abrasion test. Hence, the particles (together with FC located on the particle surface) can get detached from the fabric and reduce the water repellency.

Fabrics that were treated with FC dispersion containing a mixture of 100 nm and 15 nm sized silica particles showed a slightly higher loss in water repellency compared to fabrics treated with FC dispersions with only 15 nm sized particles, as seen when comparing tables 4.4(a) and 4.4(b). Since both the 100 nm and the 15 nm sized silica particles are

Table 4.4: Water repellency grades achieved from spray testing of fabrics treated with 5 wt% FC dispersion containing un-modified silica particles. Table 4.4(a) present results for 5 wt% FC dispersions containing silica particles with a uniform particle size of 15 nm and table 4.4(b) present results achieved from 5 wt% FC dispersions containing a mix of 15 nm and 100 nm sized silica particles. Repellency grades both before and after Martindale abrasion (5000 cycles, 12 kPa) are presented.

(a)		
wt % Si 15 nm	Water repellency before abrasion	Water repellency after abrasion
0.15	ISO 5	ISO 1
0.2	ISO 4	ISO 2
0.25	ISO 4	ISO 2

(b)		
wt % Si 15 + 100 nm	Water repellency before abrasion	Water repellency after abrasion
0.05 + 0.02	ISO 4	ISO 1
0.1 + 0.01	ISO 4	ISO 1

un-modified, exhibiting the same surface functionality, both particle sizes should form equally strong cross-links to the surface. The ratio of cross-links to particle mass is however unequal due to the large size difference between the 15 nm and the 100 nm particles, as illustrated in figure 4.3. Consequently the 100 nm particles will, due to a lower cross-links to mass ratio, more easily be abraded away from the fabric.

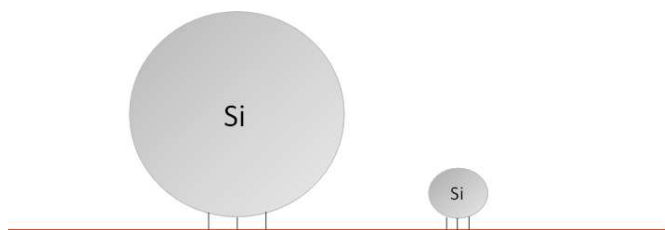


Figure 4.3: Illustration of the ratio of cross-links to particle mass.

As for oil repellency of fabrics spray treated with a 5 wt% FC dispersion containing un-modified silica particles, the PA fabric showed a somewhat higher repellency after abrasion compared to the PA/PES fabric as shown in table 4.5. Results in table 4.5 are valid for all evaluated concentrations and particle sizes of un-modified silica particles in 5 wt% FC dispersion.

Table 4.5: Oil repellency grades for PA and PA/PES fabrics spray treated with a 5 wt% FC dispersion containing un-modified silica particles. Results are valid for all evaluated concentrations and sizes of un-modified silica particles.

Fabric	Oil repellency before abrasion	Oil repellency after abrasion
PA	8	6
PA/PES	8	5

The lower repellency for treated PA/PES fabrics could indicate that the FC-dispersion is more compatible with the polyamide fibres than the polyester fibres, or that the un-modified silica particles are more willing to form cross-links to PA than to PES. The exact structure of the FC dispersion is not known, but it obviously react differently with the PA and PES polymer structures. Perhaps the ester group in PES are less prone to form cross-links to the FC compared to the amide structure in PA.

All evaluated concentrations and combinations of un-modified silica particles and FC demonstrated the same oil repellency grades. Spray treatment of pure FC dispersion without silica particles also displayed the same results. This reveals that an addition of silica particles does not affect the oil repellency achieved by the FC-dispersion. This is in agreement with previous knowledge that oil repellency can only be achieved by the FC's. The FC-concentration is high enough for all evaluated silica particle concentration to give a maximum oil repellency to the treated fabrics. Evaluations with lower FC concentrations would be interesting to find out the lowest possible FC-concentration that can introduce a maximum oil repellency grade. As previously stated, a low FC consumption is desirable both from an environmental and economical point of view.

Water spray tests performed on fabrics treated with hydrophobic silica particles and FC demonstrated that the hydrophobic functional group did not enhance the water repellency grade either before or after abrasion of treated fabrics. Comparable repellency grades were achieved for the 5 wt% FC dispersions containing hydrophobic silica particles and un-modified silica particles respectively (ISO 4 and ISO 1 before and after abrasion respectively). A chemical finish with hydrophobic silica particles and FC gave however a slightly lower oil repellency grade (7) before abrasion compared to the fabric samples treated with un-modified silica particles and FC. Abraded fabrics did however display the same repellency grades for both finishes.

When it comes to fabrics treated with FC dispersion containing reactive silica particles, repellency tests showed that the oil and water repellency grades are depend on the particle concentration. Table 4.6 demonstrates the effect of increasing silica concentrations on water and oil repellency grades for the 5 wt% FC dispersions containing reactive silica

particles. Complete wetting of all test-oils are represented by a repellency grade of '0'.

Table 4.6: Oil and water repellency grades for fabrics treated with a 5 wt% FC dispersion containing different concentrations (wt%) of reactive silica particles. Repellency grades both before and after Martindale abrasion (5000 cycles, 12 kPa) are presented.

wt % Si	Oil repellency before abrasion	Oil repellency after abrasion	Water repellency before abrasion	Water repellency after abrasion
0.5	8	6	ISO 4	ISO 2
1.5	7	6	ISO 2	ISO 1
3.0	7	1	ISO 1	ISO 1
7.0	4	0	ISO 1	ISO 1
12.0	4	0	ISO 1	ISO 1

From table 4.6 it is evident that higher concentrations of silica particles decreases both the water and oil repellent character of treated fabric. As all evaluated dispersions of reactive silica has a constant concentration of fluorocarbon, the decrease in repellency grades can be exclusively assigned to the concentration of particles. This goes against what was previously stated regarding that only FC's are able to affect the oil repelling properties of the treated fabrics. Compared to FC dispersions containing un-modified and hydrophobic silica, the FC dispersions containing reactive silica demonstrated a decrease in water repellence, before abrasion, for silica concentrations above 0.5 wt%. Silica concentrations above 3 wt% give in addition a decrease in oil repellence for the treated fabrics.

As the molecular structures in the FC-dispersion is unknown it is not possible to know whether the reactive silica particles can react with structures in the FC dispersion, already before being sprayed onto the fabrics, and thereby decrease the ability of the FC to induce oil repellence to the surface. Thus, a higher silica concentration would make it possible for a higher amount of the FC dispersion to react and thereby reduce the oil repellence. Also, if the silica particles react with elements in the FC dispersion before being applied on the textile surface the probability of achieving stronger cross-links between the particles and the textile fibres at the surface is lost. It could also be that a low concentration of silica allows for formation of a beneficial nano-on-micro surface structure that are lost, by for instance formation of large agglomerates of particles, at higher particle concentrations. Thus, according to earlier discussions on nano-on-micro surface structures, a low silica particle concentration may actually be beneficial for repellent purposes.

Results obtained in this study imply that the FC-Si treated samples had a higher oil repellency compared to the reference sample. However, the decrease in oil repellency after

abrasion was more substantial for the spray treated samples as compared to the reference fabric. The reference samples have obtained their chemical finish by foulard processing which give a higher amount of FC on the surface that is evenly distributed through the material, resulting in a high robustness which may affect the abrasion resistance. Also, the particles that are applied together with the FC-dispersion on the spray treated samples may not, as already stated, be sufficiently anchored to the fabric resulting in a loss of repellency after abrasion. Evaluations of lower numbers of abrasion cycles might give indications of how deep the spray finish penetrate into the textile material and affect the repelling properties.

A comparison of the water repellency grades before and after abrasion for FC-Si treated fabrics and the reference fabric shows that the water repellency grade after abrasion is higher for the reference (ISO 3 compared to ISO 2-ISO 1). Just as for the decrease in oil repellency, this might have to do with how the chemical finish is applied and how well the silica particles are attached to the surface.

4.5.2 Water contact angle and surface free energy

CA and SFE measurements demonstrate that spray treated samples present similar CA and SFE values as the traditionally wet treated reference fabric. Results from CA and SFE analyses of PA/PES fabrics treated with 5 wt% FC dispersions containing 15 nm sized and a mixture of 15 nm and 100 nm sized un-modified silica particles respectively are presented together with values for the reference fabric in figure 4.4. Similar values were achieved for the PA fabric.

No clear trend could be found between the values for water contact angles or surface free energies among the examined concentrations of un-modified silica in 5 wt% FC dispersion. Comparable results were achieved for samples treated with a mixture of particle sizes and samples treated with a uniform silica particle size as demonstrated in figures 4.4(a) and 4.4(b). The similarities in CA's for samples treated with two different particle sizes (15 and 100 nm) and samples treated with one particle size (15 nm) could be explained by a possible aggregation of smaller particles into larger structures. If these aggregations of small particles reach a size comparable to the 100 nm particles, similar values for the CA measurements may be achieved.

Samples treated with 5 wt% FC dispersions containing silica particle concentrations of 0.25 % Si (15 nm) and 0.1 wt% Si (15 nm) + 0.01 wt% (100 nm), respectively, displayed somewhat higher CA values as compared to the reference. The fabrics treated with 0.15 wt% Si did however display CA's closer to the CA's of the reference. These however are least affected by the abrasion than other evaluated concentrations which is a great benefit. It should however be noted that the deviations in the measurements is highly due to the rough and porous structure of the fabric surfaces.

In agreement with the CA results, the SFE measurements presents slightly better (lower)

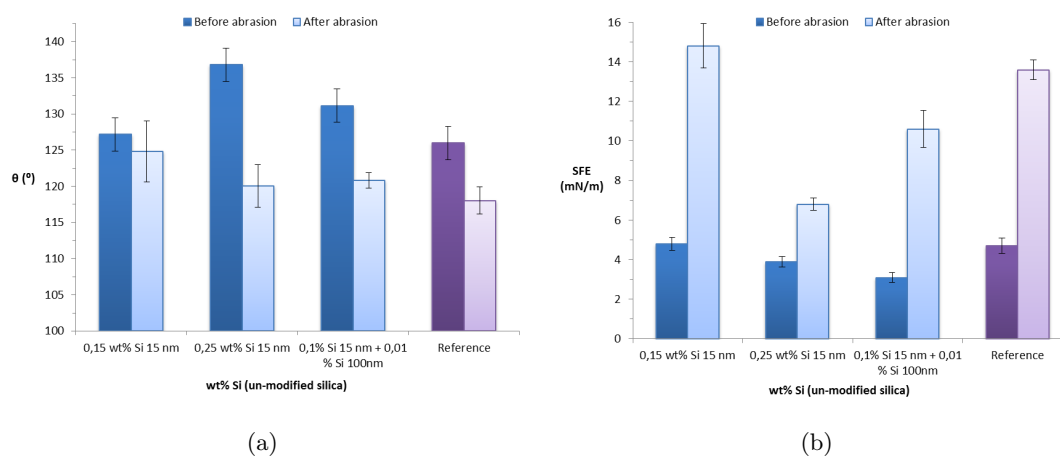


Figure 4.4: Water contact angles 4.4(a) and surface free energies 4.4(b) for PA/PES fabrics treated with 5 wt% FC dispersion containing different concentrations (wt%) of un-modified silica particles. Values both before and after Martindale abrasion (5000 cycles, 12 kPa) are presented. CA results are based on measurements of water contact angles at 3 points of the treated sample (30 values in total). SFE results are based on measurements at 3 points each for water and di-iodine-methane of the treated sample (60 values in total).

SFE values for fabric samples treated with 5 wt% FC-dispersions containing 0.25 % Si (15 nm) and 0.1 wt% Si (15 nm) + 0.01 wt% (100 nm) respectively, when comparing with reference samples. Similarly, the fabrics treated with 0.15 wt% Si show values closer to the ones of the reference as seen in figure 4.4(b). Since the SFE's are related to the CA's and calculated from the CA's and contact angles for di-iodine-methane this is however expected.

The reference fabric show values closer to the spray treated fabrics in CA and SFE measurements compared to in water and oil repellency tests. The reference fabric displayed, for instance, a higher water repellency after abrasion than FC-Si treated samples that showed a total wetting after abrasion. However, the FC-Si treated samples were able to repel the water drop in the CA/SFE experiments. The samples that have been spray treated with FC-Si dispersion obviously exhibit some degree of water repellency left after abrasion but not sufficient enough to withstand the higher pressure from the pouring water in the water repellency spray tests compared to the low pressure from the water droplet placed on the surface in the CA/SFE measurements.

Fabrics spray treated with hydrophobic silica particles in 5 wt% FC dispersion show that the CA of treated fabrics can be enhanced by modifying the silica particles with a hydrophobic functional group. CA's and SFE's for 5 wt% FC dispersions containing hydrophobic (green bars) and un-modified (blue bars) silica particles respectively are presented in figure 4.5.

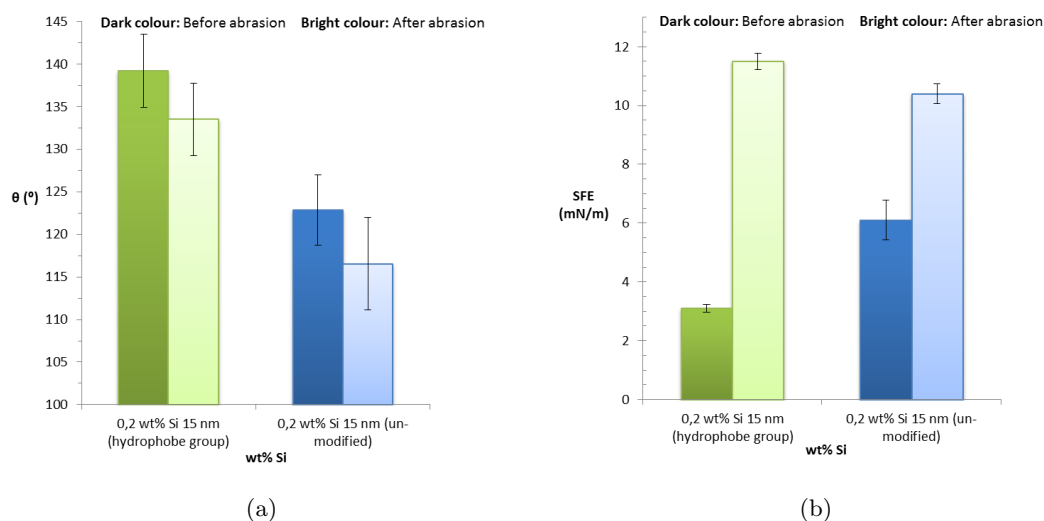


Figure 4.5: Water contact angles 4.5(a) and surface free energies 4.5(b) for PA/PES fabrics treated with 5 wt% FC dispersion containing 0.2 wt% un-modified silica particles (15 nm) (blue bars) and 0.2 wt% hydrophobic silica particles (15 nm) (green bars). Values both before and after Martindale abrasion (5000 cycles, 12 kPa) are presented. CA results are based on measurements of water contact angle at 3 points of the treated sample (30 values in total). SFE results are based on measurements of contact angles for water and di-iodine-methane at 3 points each of the treated sample (60 values in total).

In figure 4.5 it can be seen that higher CA values were obtained for fabrics treated with 5 wt% FC dispersions containing hydrophobic silica particles as compared to fabrics treated with FC dispersions holding un-modified silica particles. The hydrophobic functional group on the modified silica particles seem to add some additional repellency of water in the CA measurements. However, just as for the samples treated with dispersions of FC and un-modified silica particles, the increase in CA is not related to an higher water repellency grade in the water spray tests. The fabric samples that were treated with hydrophobic silica particles and FC displayed the same water repellency after abrasion as samples treated with un-modified silica particles and FC. The water spray tests probably give more relevant results from an application point of view, compared to the CA's, as the fabrics most likely are subjected to higher impacts in real use applications.

To possibly increase the adhesion of silica particles to the fabric, and thereby increase the abrasion resistance, FC dispersions with reactive silica particles were evaluated with various silica concentrations. The impact an increasing concentration of reactive silica particles in 5 wt% FC dispersions is illustrated in figure 4.6.

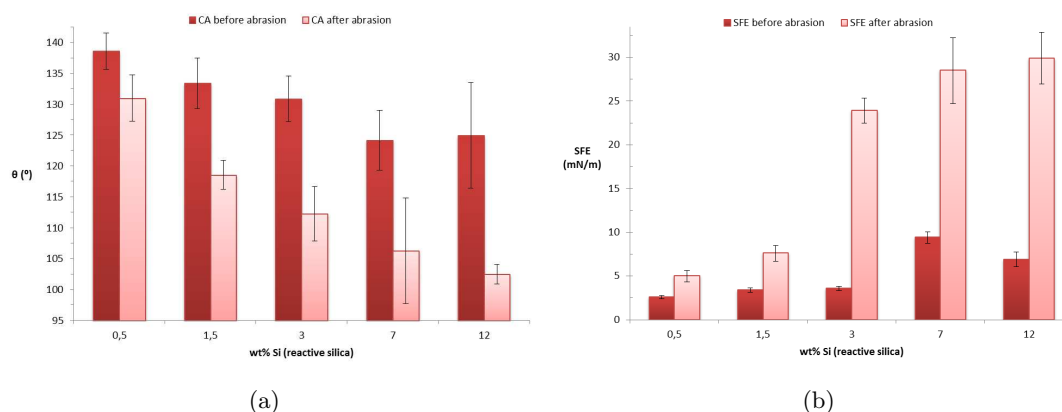


Figure 4.6: Water contact angles 4.6(a) and surface free energies 4.6(b) for PA/PES fabrics treated with 5 wt% FC dispersion containing different concentrations (wt%) reactive silica particles (7 nm). Values both before and after Martindale abrasion (5000 cycles, 12 kPa) are presented. CA results are based on water contact angle measurements at 3 points of the treated sample (30 values in total). SFE results are based on contact angle measurements of water and di-iodine-methane at 3 points each of the treated fabric (60 values in total).

As can be seen in figure 4.6, higher silica concentrations show a decrease in CA together with an increase in SFE. The change in both CA's and SFE's, after Martindale abrasion, increases steadily with an increase in silica concentration. Again, a low particle concentration seem to be beneficial. As stated earlier, the decrease in CA at higher concentrations of silica particles might be due to loss in surface structure as the particles may diminish the natural roughness of the textile surface.

All in all, a low concentration of silica particles seem to be beneficial for repelling properties of textiles. This is contrary to results achieved by Nimitrakoolchai et al.[31]. In their studies regarding SiO_2 coatings on glass surfaces they concluded that higher particle concentrations give increased surface roughness and CA's. However, since their work is based on coatings of smooth glass surfaces in contrast to the rough textiles used in this study, it is difficult to draw any conclusions. The textile fibres in them selves have a micro sized structure which should contribute to the nano-on-micro surface structure that is sought after on repellent surfaces.

Hence, it might be possible that only a low amount of particles is required to create a suitable surface structure as the textile material by it selves contribute to one length scale. Also, the silica particles used in the study performed by Nimitrakoolchai et al. were un-modified and did not have any reactive functional group. If the particles that exhibit a reactive group can induce a reaction with some structures in the FC dispersion before being applied onto the surface the repellent effect of the FC might get lost, affecting the CA and SFE.

4.6 Plasma treatment

Plasma treatment of fabric samples were performed, in addition to spray treatment with FC-Si dispersions, with intention to increase the adhesion of silica particles and fluorocarbons. A better adhesion of chemicals might increase the abrasion resistance of the spray treated fabrics. Plasma was evaluated as both a pre- and post treatment, as the reaction routes for the two types of treatments are potentially different. A plasma pre-treatment results in an activation of the fabric surface which may result in binding of subsequent chemicals. A plasma post-treatment on the other hand, may induce cross-linkings and other plasma related chemical reaction between the applied chemicals.

4.6.1 Treatment time and treatment power

CA values for PA/PES fabrics spray treated with a dispersion of 5 wt% FC and 0.2 wt% un-modified silica particles (15 nm) and plasma treated at different powers and times are presented in figure 4.7. As can be seen in the figure, a power of 280 W seem to generate the highest CA's after abrasion. The deviations in the results is though relatively large due to difficulties in measurements related to the rough and porous structure of the textiles. It is therefore difficult to draw conclusions of which treatment power, or treatment time, that would give the best results.

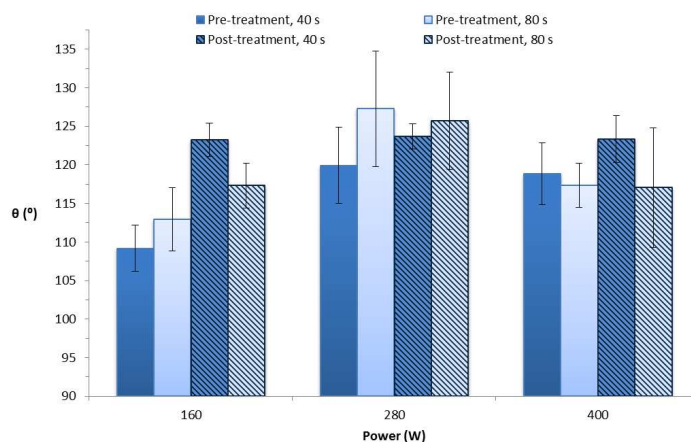


Figure 4.7: Water contact angles after Martindale abrasion (5000 cycles, 12 kPa) for PA/PES fabrics treated with 5 wt% FC dispersion containing 0.2 wt% un-modified silica (15 nm). Results for both pre-treatments (bars with uniform colour) and post-treatments (striped bars) at different plasma treatment powers and treatment times are presented. All samples displayed similar CA's before the abrasion (CA: $126.5 \pm 2^\circ$). Results are based on measurements at 3 points of the treated sample (30 values in total).

It is known from earlier published work that the highest treatment power is not always the most efficient. Plasma has an etching effect on the material which increases with

increasing treatment powers. Thus, a too high treatment power might destroy the surface structure instead of enhance it. Therefore, an higher CA's at a power of 280 W compared to a power of 400 W could be reasonable. Evaluations performed on treated PA fabric did not show as clear results as those for treated PA/PES fabric therefore the choice of treatment power and treatment time is based on results achieved for the treated PA/PES fabric.

Surface free energy evaluations indicate that the lowest values were achieved at a power of 280 W, see figure 4.8. Both a pre-treatment of 80 seconds and post-treatment of 40 seconds at 280 W gave low SFE's. A low SFE value was also achieved for a 40 second post-treatment at a power of 160 W. However, both CA and SFE measurements were slightly better for the 280 W treatments, hence the most effective power, among the evaluated plasma powers, seem to be 280 W.

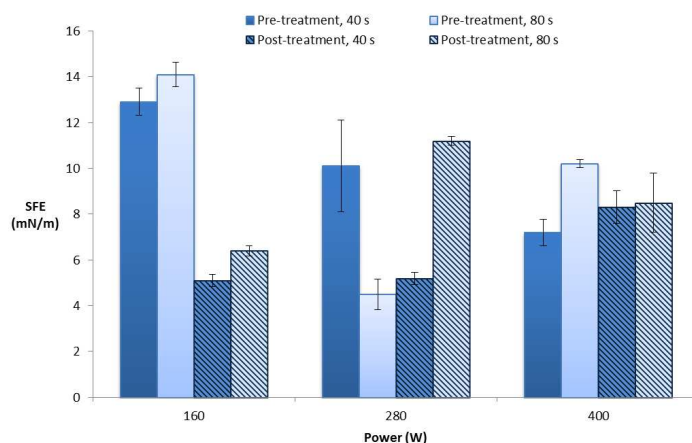


Figure 4.8: Surface free energies after Martindale abrasion (5000 cycles, 12 kPa) for PA/PES fabrics treated with 5 wt% FC dispersion containing 0.2 wt% un-modified silica (15 nm). Results for both pre-treatments (bars with uniform colour) and post-treatments (striped bars) at different plasma treatment powers and treatment times are presented. All samples displayed similar SFE's before abrasion (SFE: 4.5 ± 0.7 mN/m). Results are based on measurements at 3 points each for water and di-iodine-methane of the treated sample (60 values in total).

As no significant differences could be seen between the plasma pre-treated and plasma post-treated samples, the choice of whether to use a pre- or post-treatment was instead based on an health perspective. Fluorocarbons are able to form toxic hydrogen fluoride gas (HF) when they are heated. The reactions that form during plasma treatment are unknown hence to reduce the risk of producing toxic bi-products the pre-treatment alternative was chosen.

4.6.2 Impact of plasma activation on hydrophobicity and oleophobicity

The hydrophobic and oleophobic character of plasma treated fabrics (spray treated with FC-Si dispersion) was evaluated using the same standardised water and oil repellency tests as for un-plasma treated fabrics. Plasma treatment does not seem to affect either the hydrophobicity or the oleophobicity of the fabric samples spray treated with un-modified Si-particles and FC dispersion as shown in tables 4.7 and 4.8. The textile samples showed the same repellency grades both with and without plasma treatment. The repellency grades after abrasion was not affected by the plasma treatment either.

Table 4.7: Oil repellency grades for PA and PA/PES fabrics spray treated with a 5 wt% FC dispersion containing un-modified silica particles. Results are presented for both plasma treated and un-plasma treated samples and are valid for all evaluated concentrations and sizes of un-modified silica particles. Repellency grades both before and after Martindale abrasion (5000 cycles, 12 kPa) are presented.

Fabric	Oil repellency	Oil repellency	Oil repellency	Oil repellency
	before abrasion	after abrasion	before abrasion	after abrasion
	with plasma	with plasma	without plasma	without plasma
PA	8	6	8	6
PA/PES	8	5	8	5

A reason for this could be that the chemical cross-links formed between the hydroxyl-groups on the un-modified silica particles and the activated textile surface are too weak to withstand the impact of the abrasion. Evaluation of different abrasion times and loads could answer if that is the case. Similar results were achieved for samples treated with dispersions containing hydrophobic silica particles and FC. Plasma treatment did not affect the repellent character of these treated samples either.

Unlike the FC dispersions containing either un-modified or hydrophobic silica particles, the FC dispersions with reactive particles seem to be more positively affected by the plasma pre-treatment. Plasma activation enhances both the water and oil repellency before abrasion as demonstrated in tables 4.9 and 4.10. This enhancement in liquid repellency could be an indication of plasma induced cross-links, which is an expected result due to the higher reactivity of these silica particles.

The effect is not as substantial after abrasion but two of the evaluated concentrations showed higher oil repellency grades for FC-Si spray treated fabrics that have been plasma pre-treated compared to un-plasma treated fabrics. Table 4.9 shows that the oil repellency after abrasion increased from 1 to 3 for the sample treated with 3 wt% reactive silica and FC and from 0 to 1 for the 7 wt% sample. The best repellency was achieved using the lower concentrations of 0.5 and 1.5 wt% reactive silica in FC dispersion.

Table 4.8: Water repellency grades achieved from spray testing of fabrics treated with 5 wt% FC dispersion containing un-modified silica particles with and without plasma pre-treatment. Tables 4.8(a) and 4.8(b) present results for 5 wt% FC dispersions containing silica particles with a uniform particle size of 15 nm and a mix of 15 nm and 100 nm sized silica particles respectively. Repellency grades both before and after Martindale abrasion (5000 cycles, 12 kPa) are presented.

(a)				
wt % Si	Water repellency before abrasion with plasma	Water repellency after abrasion with plasma	Water repellency before abrasion without plasma	Water repellency after abrasion without plasma
0.15	ISO 5	ISO 1	ISO 5	ISO 1
0.2	ISO 4	ISO 2	ISO 4	ISO 2
0.25	ISO 4	ISO 2	ISO 4	ISO 2

(b)				
wt % Si	Water repellency before abrasion with plasma	Water repellency after abrasion with plasma	Water repellency before abrasion without plasma	Water repellency after abrasion without plasma
0.05 + 0.02	ISO 4	ISO 1	ISO 4	ISO 1
0.1 + 0.01	ISO 4	ISO 1	ISO 4	ISO 1

Table 4.9: Oil repellency grades for PA/PES fabrics treated with 5 wt% FC dispersion containing different concentrations (wt%) reactive silica particles. Repellency grades both before and after Martindale abrasion (5000 cycles, 12 kPa) are presented for plasma treated and un-plasma treated fabrics.

wt % Si	Oil repellency before abrasion with plasma	Oil repellency after abrasion with plasma	Oil repellency before abrasion without plasma	oil repellency after abrasion withouth plasma
0.5	8	6	8	6
1.5	8	6	7	6
3.0	7	3	7	1
7.0	6	1	4	0
12.0	6	0	4	0

Water repellency was generally better with plasma activation than without as shown in table 4.10. However the effect was lost after abrasion. As discussed earlier, a reaction between the reactive silica particles and the FC dispersion might reduce the repellency grades. It would therefore be interesting to examine if similar results would be achieved if the fabrics were treated a dispersion containing only reactive silica particles before applying of the FC dispersion. This might answer if the plasma activated surfaces are more likely to induce a reaction of reactive silica particles compared to un-modified silica particles.

Table 4.10: Water repellency grades for PA/PES fabrics treated with wt% FC dispersion containing different concentrations (wt%) of reactive silica particles. Oil repellency grades both before and after Martindale abrasion (5000 cycles, 12 kPa) are presented for plasma treated and un-plasma treated samples.

wt % Si	Water repellency	Water repellency	Water repellency	Water repellency
	before abrasion with plasma	after abrasion with plasma	before abrasion withouth plasma	after abrasion withouth plasma
0.5	ISO 4	ISO 2	ISO 4	ISO 2
1.5	ISO 3	ISO 1	ISO 2	ISO 1
3.0	ISO 2	ISO 1	ISO 1	ISO 1
7.0	ISO 2	ISO 1	ISO 1	ISO 1
12.0	ISO 2	ISO 1	ISO 1	ISO 1

4.6.3 Impact of plasma activation on water contact angle and surface free energy

Analyses of CA and SFE for fabrics treated with 5 wt% FC dispersion containing un-modified, 15 nm sized silica particles showed some differences in CA and SFE values when comparing plasma treated and un-treated samples, see figure 4.9.

As can be seen in figure 4.9(a), plasma treatment seem to increase the CA's of treated fabrics slightly before abrasion. This might be an indication that the plasma treatment increases the amount of silica particles on the fabric surface by formation of cross-links between the hydroxyl-groups on the silica particles and the textile fibres. Also it might be that plasma activation induce some cross-linking reactions between the particles applied on the fabric surface. The deviation of the values for plasma treated samples and samples that have not been plasma treated is however overlapping. More extensive analyses are therefore needed to get more reliable results.

SFE measurements of plasma treated samples show, in agreement with CA evaluations, a

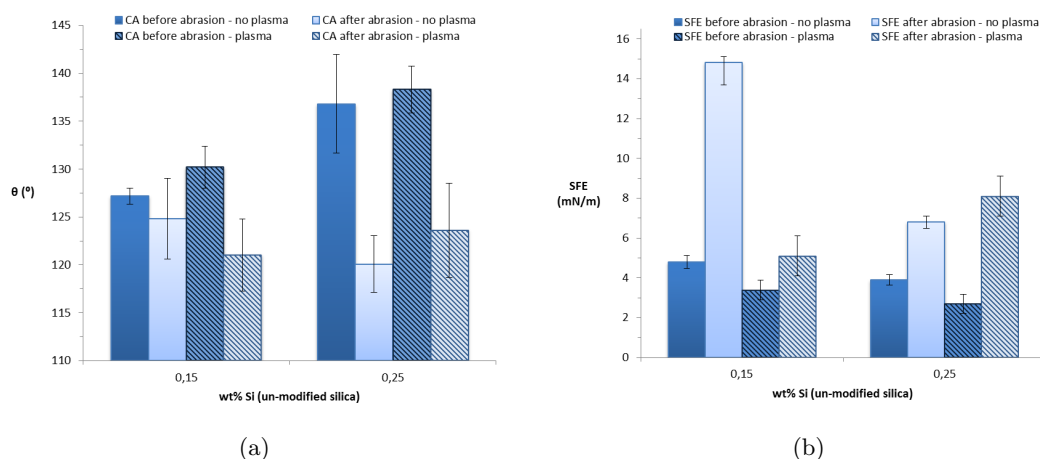


Figure 4.9: Water contact angles 4.9(a) and surface free energies 4.9(b) for PA/PES fabrics treated with 5 wt% FC dispersion containing two different concentrations of 15 nm sized un-modified silica particles (0.15 and 0.25 wt%). Values both before and after Martindale abrasion (5000 cycles, 12 kPa) are presented for both plasma treated samples (striped bars) and un-plasma treated samples (un-striped bars). CA results are based on measurements of water contact angle at 3 points of the treated sample (30 values in total). SFE results are based on measurements of water and di-iodine-methane contact angles at 3 points each of the treated sample (60 values in total).

modest improvement in the results before abrasion. Plasma treated fabrics display somewhat lower SFE values in comparison to samples that have not been plasma treated as shown in figure 4.9(b). It could however be discussed whether the difference in SFE between plasma activated fabrics and fabrics without plasma activation is of much importance as both fabrics display similar water and oil repellence.

Values from CA and SFE measurements of plasma activated and non-activated fabrics, spray treated 5 wt% FC dispersion containing a mixed particle sizes of un-modified silica, are illustrated in figure 4.10.

From SFE analyses of samples treated with a FC dispersion with mixed silica particle sizes (0.1 wt% 15 nm sized + 0.01 wt% 100 nm sized un-modified silica particles), presented in figure 4.10(b), the SFE values after abrasion seem to increase somewhat more for plasma treated samples. The difference in values for plasma activated samples and samples that have not been plasma treated is however not that substantial. As mentioned above, no effect can be seen on the water or oil repellency grades. Measured values of CA displayed a similar trend for these mixed size dispersions as FC dispersions holding a uniform silica particle size of 15 nm as presented in figure 4.10(a). Hence, it could be concluded that a mixture of different particle sizes does not seem to have any significant effect on either the CA or the SFE values for fabrics treated with FC-Si

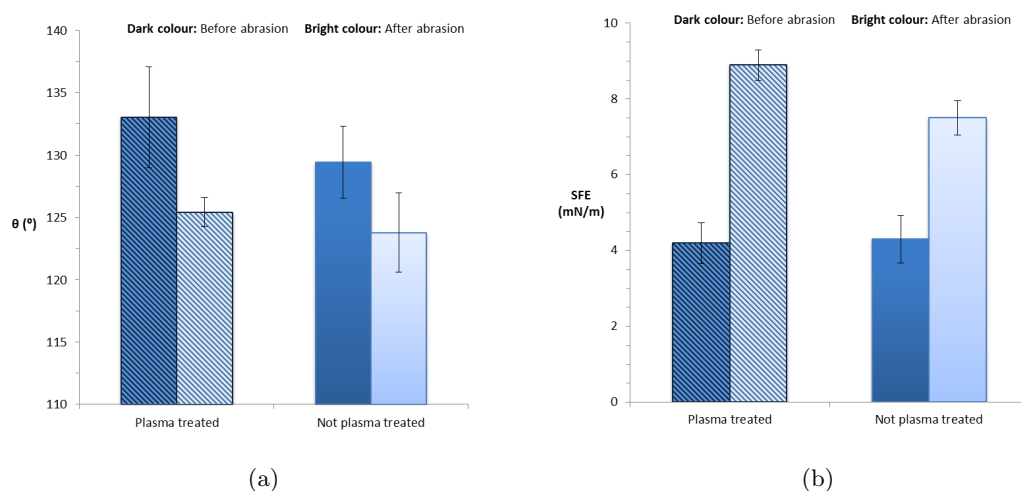


Figure 4.10: Water contact angles (4.10(a)) and surface free energies (4.10(b)) for PA/PES fabrics treated with 5 wt% FC dispersion containing a mix of 15 nm and 100 nm un-modified silica particles (0.1 wt% 15 nm Si + 0.01 wt% 100 nm Si). Values both before and after Martindale abrasion (5000 cycles, 12 kPa) are presented for both plasma treated (striped bars) and un-plasma treated (un-striped bars) samples. CA results are based on measurements at 3 points of the treated sample (30 values in total). SFE results are based on water and di-iodine-methane contact angles at 3 points each of the treated fabric (60 values in total).

dispersions.

Fabric samples treated with a dispersion of hydrophobic silica and FC did not display any substantial differences in water contact angles or surface free energy for plasma treated and untreated samples as can be seen in figure 4.11.

At a concentration of 0.2 wt% silica, a hydrophobic functional group on the silica particles seem to enhance the CA's both before and after Martindale abrasion for both plasma activated and un-activated samples. The plasma treatment seem to affect both hydrophobic and un-modified silica particles in the same way. However, analyses of the SFE after abrasion, figure 4.11(b), displayed higher SFE values for plasma activated samples treated with hydrophobic particles compared to un-modified particles (both particle types in FC dispersion).

As already mentioned in section 4.6.2, the reactive silica particles seems to be positively affected by the plasma activation. The impact of plasma treatment for different concentrations of silica particles with a reactive group are presented in figures 4.12 and 4.13. In agreement with results achieve for un-modified silica particles, it seems that the plasma treatment increases the CA and decreases the SFE before abrasion indicating a higher

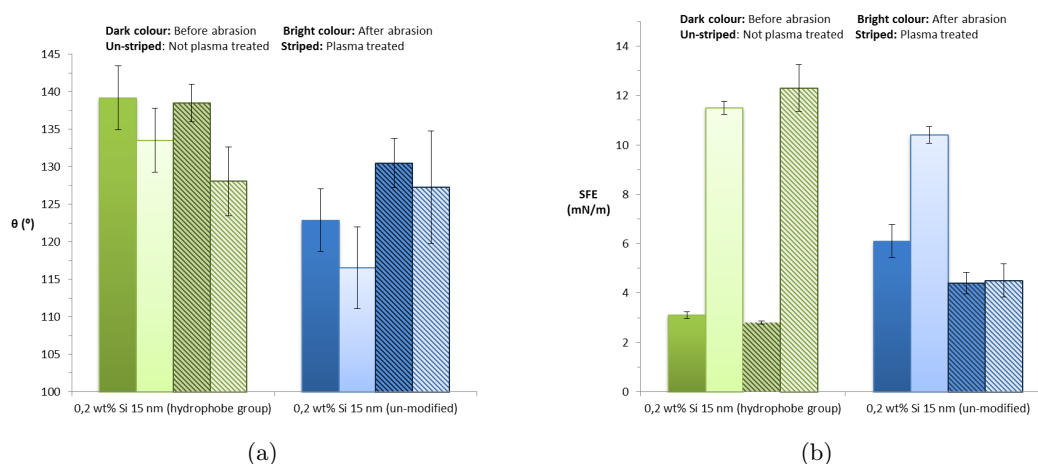


Figure 4.11: Water contact angles (4.11(a)) and surface free energies (4.11(b)) for PA/PES fabrics treated with 5 wt% FC dispersion containing un-modified silica particles (blue bars) and hydrophobic silica particles (green bars) at a concentration of 0.2 wt%. Results both before and after Martindale abrasion (5000 cycles, 12 kPa) are presented for both plasma treated (striped bars) and un-plasma treated (un-striped bars) samples. CA results are based on water contact angle measurements at 3 points of the treated sample (30 values in total). SFE results are based on water and di-iodine-methane contact angle measurements at 3 points each of the treated fabric (60 values in total).

amount of attached particles at the surface.

The effect is more substantial at higher concentrations of reactive silica as can be interpreted from both figures 4.12 and 4.13. These results also indicate that a lower particle concentration seem to display better CA's and SFE's both before and after abrasion compared to higher silica concentrations, which is the same trend as has been previously seen.

A summary of the CA's and the SFE's for the different types of silica particles, in 5 wt % FC-dispersion, evaluated in this study are presented in figures 4.14 and 4.15. All values, are received from plasma pre-treated samples of PA/PES fabric. Values for the plasma activated and FC-Si spray treated fabrics are compared to an industrially used reference fabric produced by FoV Fabrics. Results from CA and SFE measurements are presented with values before and after and after Martindale abrasion (5000 cycles, 12 kPa) as dark and bright bars respectively.

Comparing the CA's before abrasion, dark-coloured bars, in figure 4.14 it is clear that functionalised silica particles in combination with FC dispersion show reasonably higher CA's before abrasion as opposed to fabric samples spray treated with FC dispersions containing un-modified silica particles (blue bars) and fabrics that are only treated with

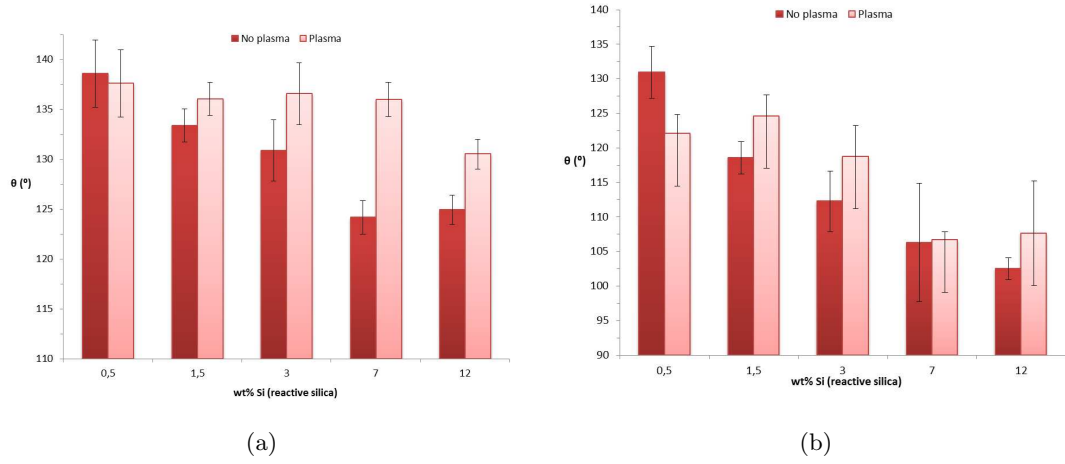


Figure 4.12: Water contact angles for PA/PES fabrics treated with 5 wt% FC dispersion containing 7 nm sized reactive silica particles of different concentrations (wt%). Results both before (4.12(a)) and after (4.12(b)) Martindale abrasion (5000 cycles, 12 kPa) are presented for plasma treated (striped bars) and un-plasma treated (un-striped bars) samples. CA results are based on measurements at 3 points of the treated sample (30 values in total).

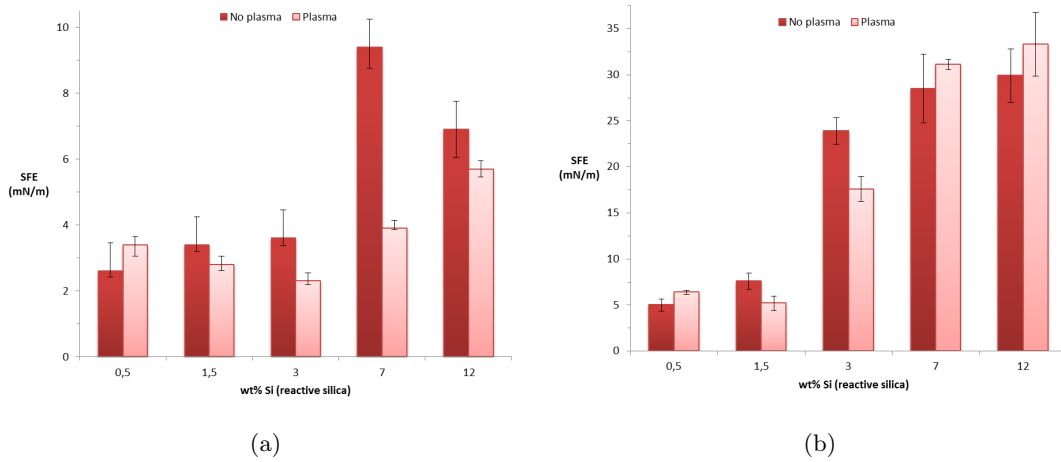


Figure 4.13: Surface free energies for PA/PES fabrics treated with 5 wt% FC dispersion containing 7 nm sized reactive silica particles of different concentrations (wt%). SFE values both before (4.13(a)) and after (4.13(b)) Martindale abrasion (5000 cycles, 12 kPa) are presented for plasma treated (striped bars) and un-plasma treated (un-striped bars) samples. Results are based on measurements at 3 points each for water and di-iodine-methane of the treated sample (60 values in total).

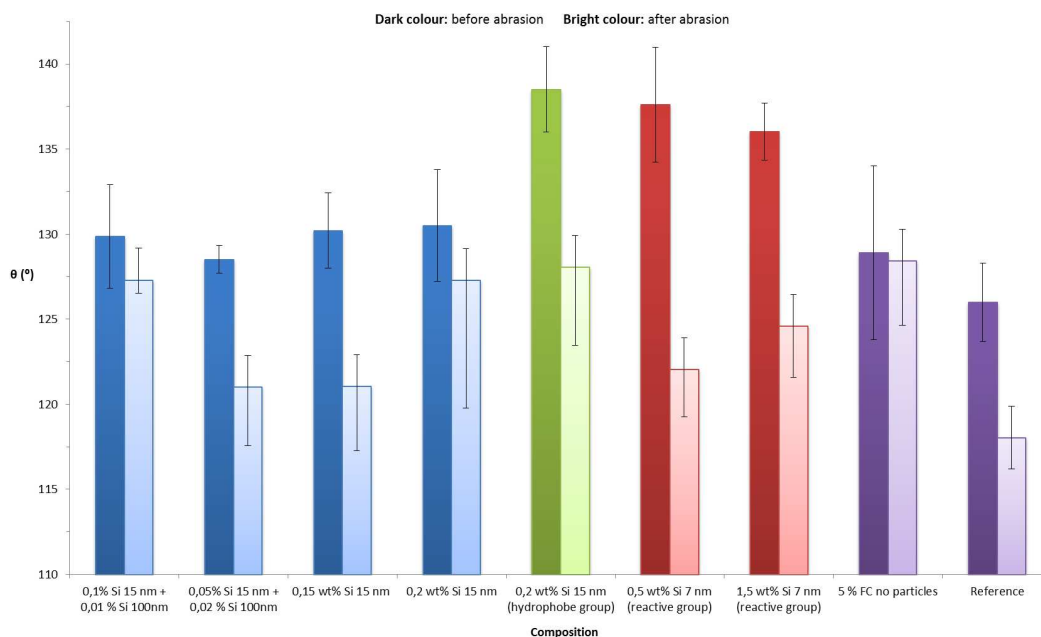


Figure 4.14: Water contact angles for plasma treated PA/PES fabric treated with 5 wt% FC dispersion and different compositions of silica particles. Values for the referent sample also included. CA's both before and after Martindale abrasion (5000 cycles, 12 kPa) are presented. Blue bars shows samples with un-modified Si-particles, green and red bars shows sample with hydrophobic and reactive silica particles respectively and purple bars shows samples without silica particles. Results are based on measurements at 3 points of the treated sample (30 values in total).

FC dispersion (purple bars). CA measurements of abraded samples does however display a higher decrease in CA values for these modified particles resulting in comparable CA's, after abrasion, for more or less all evaluated samples. This indicates that the modified particles are more easily anchored to the textile surface giving a higher coverage of particles at the surface and consequently higher CA before abrasion. However, these results also states that, just as for the un-modified silica particles, the bonds or cross-links that might form between the particles and the textile fibres are not strong enough to withstand the impact of Martindale abrasion at the tested parameters.

The reference sample displayed lower CA both before and after abrasion as compared to spray treated samples (both with and without particles). Including results from water repellency tests (were the reference sample showed higher repellency after abrasion compared to spray-treated samples), it can however not be concluded that the reference sample has a lower abrasion resistance.

The fabric that was only treated with 5 wt% FC dispersion (no particles) seem to show

the smallest decrease in CA after abrasion, see purple bars second most to the right in figure 4.14. This lower decrease in CA after abrasion, for samples treated without silica particles, might be due to lost of FC attached to particles for FC-Si treated samples. It might also be due to a generally higher adhesion between the fabric and the FC as compared to between the silica particles and the FC. The commercially FC's that are utilized in this project are designed especially for textile materials. Altering the textile surface may therefore require a change of FC.

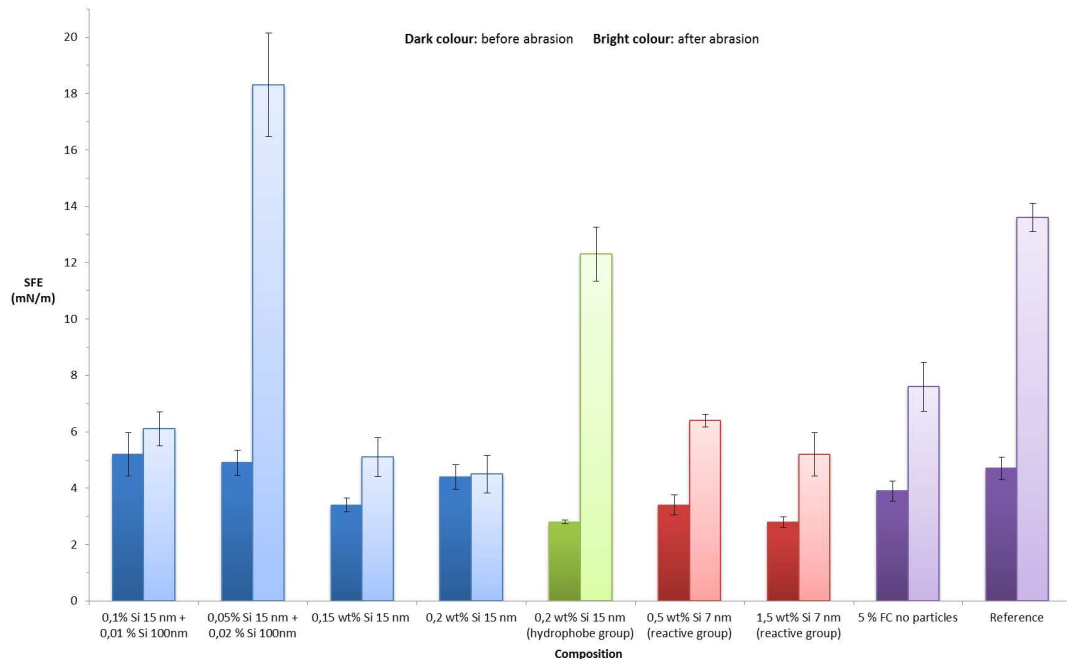


Figure 4.15: Surface free energies for plasma treated PA/PES fabric treated with 5 wt% FC dispersion and different compositions of silica particles. SFE's both before and after Martindale abrasion (5000 cycles, 12 kPa) are presented. Values for reference sample also included. Blue bars shows results for samples treated with with un-modified silica particles, green and red bars shows results for sample treated with hydrophobic and reactive silica particles respectively and purple bars shows samples without silica particles. Results are based on measurements at 3 points each for water and di-iodine-methane of the treated sample (60 values in total).

Results from SFE tests of the for different compositions of silica particles and FC together with the reference sample are shown in figure 4.15. The SFE values follow the same trend as the CA's with slightly better values before abrasion for samples treated with dispersions of functionalised silica particles and FC. The increase in SFE after abrasion is however most substantial for the hydrophobic silica particles, shown by the green bars in the middle of figure 4.15.

Before the evaluations, the hypothesis was that silica particles functionalised with a reactive group would be more prone to create chemical bonds to fibres at the textile surface compared to un-modified or hydrophobic Si-particles. Before abrasion, it has been seen that samples treated with FC dispersions containing reactive particles give better repellent properties compared to samples treated with un-modified particles in FC. However, after abrasion the repellent effect is lost to the same level as for samples treated with un-modified silica particles. Thus, even with the more reactive functional groups attached, the reactive particles do not seem to be able to create adequate bonds to the textile fibres.

Analyses performed in this study do not, however, display either higher repellency grades or better CA/SFE values for the fabrics treated with FC-dispersion including reactive particles which could indicate a higher deposition of particles and FC on the surface. Reasons could be a reaction between silica particles and FC in the dispersion or that plasma activation with oxygen does not create suitable reactive sites on the fabric. Evaluations of plasma activation with other types of process gases might give different results as other types of reactive sites might be formed.

5

Conclusions and future studies

TRADITIONAL CHEMICAL FINISHING of textiles might have gotten competition. A combination of plasma activation and a spraying process could be a more environmentally friendly and less costly alternative to the traditional wet finishing of textiles.

Results from this study implies that it is possible to enhance the water contact angles and the water and oil repellency by combining fluorocarbon dispersions with silica particles. Results also imply that higher repellency grades can be achieved by using lower concentrations of silica and fluorocarbon as compared to higher concentrations. A FC-concentration of 5 wt% is sufficient to induce maximum oil repellency to treated fabrics. Evaluations with lower FC concentrations could be interesting to find out the lowest possible FC-concentration that can introduce a maximum oil repellency grade.

A mixture of different particle sizes does not increase the repelling effect or the water contact angles of Si-FC spray treated fabrics. A possible aggregation of smaller particles could be an explanation. A hydrophobic or reactive modification of the silica particles can, however, increase water contact angles and lower surface free energies. Abrasion of fabrics affect finishes of silica and fluorocarbon dispersion to a higher extent as compared to finishes of pure fluorocarbon dispersion. It is obvious that the silica particles, unmodified or modified, does not form strong enough cross-links to the textile fibres.

Spray treatment as such does not form as durable finishes as traditional wet finishing, but it consumes less chemicals. Therefore, the choice of finishing method will, for producing companies, be a balance between finishing durability/effect and economical/environmental issues.

Plasma activation increases water contact angles implying a higher deposition of silica

particles and fluorocarbons on the surface. Plasma activation does, however, not increase the adhesion of silica particles enough to avoid loss of particles during abrasion. Plasma activation prior application of dispersions containing fluorocarbons and reactive Si-particles increases water contact angles and repellency grades. The results seem though to be concentration dependent. Therefore, in future studies trials with other types of reactive particle dispersions would be interesting. Also, trials where a dispersion of reactive particles are applied separately before the FC dispersion should be performed to investigate whether the FC dispersion interfere with reactions between active sites on the fabric and the reactive silica particles.

Further, it would be interesting to investigate the effect of process parameters such as the electrode distance during treatment or the choice of process gas. Investigations of whether other plasma surface modifications could enhance the durability of chemical finishes could be performed. For instance, if addition of aerosols, containing reactive particles, in the plasma zone or plasma polymerisation with monomer can create structures of suitable sizes on the textile surface, plasma treatment could potentially substitute the silica dispersions.

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