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Durable Oil and Water Repellent Outdoor Fabrics by Atmospheric PlasmaTreatment

Reducing the use of perfluorinated compounds

KBTX05 Master of Science Thesis in Chemical and Biological Engineering

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Cover image: Droplets of paraffin oil on polyamide fabric treated with fluorocarbons

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ABSTRACT

Water and oil repellency are of great importance in outdoor garments to protect the wearer from the surrounding environment. The conventional methods used for impregnation of textiles, to gain the repellency effect, consume huge amounts of chemicals and energy. New methods are sought for that can reduce this consumption. The only known compounds that have a low enough surface energy to provide oil repellency are fluorocarbons. But the use of fluorocarbons is connected with negative effects on the environment and human health and it is therefore desirable to lower the use of these chemicals.

This diploma work is focused on the perfluorinated compounds that are used in outdoor garments to give them oil and water repellent properties. Atmospheric plasma treatment has been evaluated as a method to reduce the amount of fluorocarbons that is needed to gain oil and water repellency of polyamide fabrics. The effect of the plasma treatment on the endurance of the fluorocarbon finish towards washing has been investigated. Atmospheric plasma was used as a pre-treatment before application of the fluorocarbon finish through a conventional wet chemical treatment. The effect of the plasma treatment was evaluated with standard test methods for water repellency and oil repellency. Contact angle measurements were also performed for evaluation.

It could be seen that the plasma treatment increased the ability of the fluorocarbon finish to withstand washing, due to stronger bonding between fabric and finish. The treatment also made it possible to reduce the chemical content to one third while retaining the same repellency grades. It was also found that contact angle measurements could be used to detect differences between samples that obtained the same grades from the water spray test and the oil repellency test.

Key words: Plasma treatment, fluorocarbons, textile finish, washing durability, hydrophobicity, oleophobicity

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Anna Hedegärd, Göteborg 2014-05-22

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1. INTRODUCTION

Textiles are of great importance in society in a wide variety of applications. It ranges from clothing and interior textiles to medical implants and wearable electronics [1].When it comes to clothing, a property that is important in everyday life is water repellency.

The ability of a garment to protect from the weather has been important for thousands of years. Leather was probably the first material to be used for this purpose. Fabrics were first coated with, for instance, wax and animal fat to gain water repellency [2]. Today there is a high demand for functional textiles showing oleophobic and hydrophobic characteristics e.g. oil and water repellency. Oleophobic behavior is important since it contributes to the soil repellency of a garment. A number of different ways have been used to render water repellent fabrics and nowadays it is important that the garments not only show the desired hydrophobicity, but also are comfortable to wear. It is possible to make fabrics with excellent water and oil repellency by using perfluorinated compounds, which are used in industry today. Fluorinated compounds are the only known substances that can give the textiles oleophobic characteristics. However, these compounds have been shown to be hazardous for both human health and the environment. They have been found in locations far from any source, which shows that they are persistent. They have also been detected in human blood across the world and have been found to be endocrine disrupting [3]. It is therefore of great concern to find less harmful alternatives or to find new methods to reduce the use of these substances.

Plasma treatment is a method that might help reducing the amount of fluorocarbons needed to withhold the hydrophobic and oleophobic behavior of fabrics. In the traditional wet chemical process the fabric is immersed in the chemical solution, thus the entire fabric is impregnated. With plasma treatment, on the other hand, the surface can be treated while the bulk is remained unchanged. Plasma treatment modifies the surface chemically allowing stronger bonding between textile and finish [4]. Hence, the chemical quantities can be reduced while the desired properties are still obtained. In this study the plasma treatment will be combined with a wet chemical treatment, although if it can be verified that the plasma treatment have a positive effect it could be combined with another finishing technique to reduce the environmental impact.

This master thesis project was conducted at Swerea IVF and is a part of the Formas-financed project SUPFES. The aim of the SUPFES project is to find alternatives to the fluorocarbons that are used in textile industry today. Within the project, researchers will evaluate the risks linked to different chemicals used for textile finishing and also investigate if they provide a sufficient technical performance in terms of water and soil repellency [5].

1.1 Aim

The aim of this project is to use atmospheric plasma treatment on polyamide fabrics and investigate if it can lead to a reduction of the amount of perfluorinated compounds needed to withhold water and oil repellency. The focus will be on the washing durability of the impregnation.

Atmospheric plasma treatment will be compared to the conventional method for impregnating fabrics. The effect of reducing concentrations of the chosen fluorocarbon will be studied and combinations of fluorocarbon (FC) and fluorocarbon-free compounds will be compared. Oil and water repellency will be tested before and after ageing of the fabrics.

2. THEORETICAL BACKGROUND

This chapter will describe the theoretical background that is essential for this study. It will begin with a description of textile fibers and fabrics. Polyamides, which are the kind of fiber used in this study, will be described shortly. The methods to gain water repellency in textiles will be explained and the theory of hydrophobicity and oleophobicity will be described. Chemicals used for water and oil repellent finishing will be presented and conventional wet chemical treatment will be described. Finally, the concept of plasma treatment will be explained.

2.1 Textiles

For centuries only natural fibers like cotton, wool and silk were used for textile production. In the end of the nineteenth century the first ‘man-made’ fibers were manufactured. They were based on cellulose. The first synthetic polymers to be used commercially were polyesters and polyamides. Natural fibers exist mostly as staple fibers, which mean that they are 2-50 cm in length. To convert the staple fibers into a yarn they need to have some roughness so that they are able to adhere to each other. Synthetic fibers are instead long, continuous filaments [6].

In woven textile fabrics there is a distinction between the threads in the two directions, which are called the warp and weft directions. For instance, there can be a difference in thickness between warp threads and weft threads. The warp threads, referred to as ends, run down the length of the fabric and the weft threads, called picks, run from side to side. This is illustrated in figure 1.

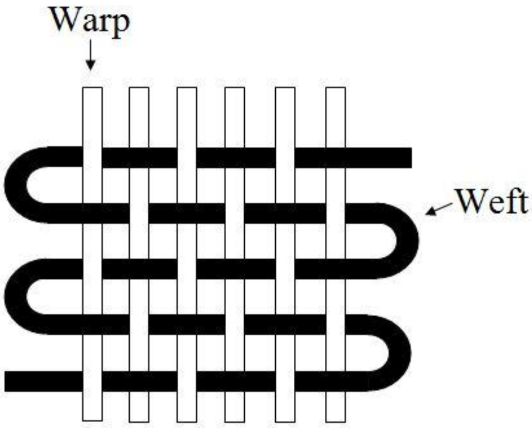

Figure 1: Illustration of the threads in warp and weft directions

The ends and picks create a weave. There are a great number of possible weaves and it influences both appearance and behavior of the fabric [7]. In the simplest weaves, called plain weaves, there are single threads in both warp and weft direction. A pick will pass over one end, then under the next and so on, as illustrated in figure 1. The woven structure of the fabric affect the roughness of the surface and hence the repellency behavior [8].

2.2 Polyamide fibers

Polyamides were one of the first kinds of synthetic polymers that were used in fiber applications, like textiles. In polyamides there is an amide linkage between the repeating units. The most common polyamides used for fiber applications are PA6 and PA66, due to their good flexibility, tensile strength and abrasion resistance [9]. The structure of PA6 and PA66 can be seen in figure 2.

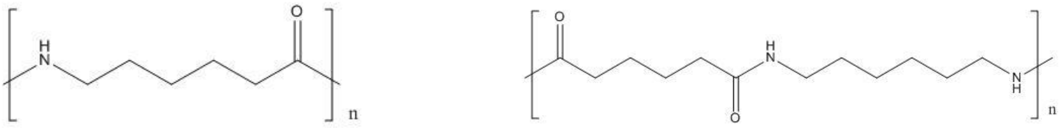

Figure 2: Structure of PA6 (left) and PA66 (right)

A number of studies have described adhesion improvement of polyamide using atmospheric plasma treatment [10, 11, 12, 13]. Pappas et al used atmospheric plasma to modify the surface of polyamide films and fibers to improve the wettability. This was done in order to investigate if the plasma treatment could be used to improve, for example, adhesion. They showed that the plasma treatment increased the hydrophilicity of the surface and gave a stable wetting behavior [10]. Iriyama et al used low temperature fluorocarbon plasma at vacuum to render a hydrophobic finish on polyamides. After 30 minutes of laundering they evaluated the hydrophobicity by contact angle, roll-off angle and breakthrough water pressure measurements. They found that treatment with saturated fluorocarbons gave better durability to the surface than treatment with unsaturated fluorocarbons. They could also conclude that the drying conditions are important for the water repellency after washing; high temperatures were needed to retain the repellency effect [14].

2.3 Water repellency in textiles

Water repellency is an important characteristic of outdoor garments. For waterproof garments a laminate or coating is sometimes applied to the inside of the fabric, it acts as a barrier towards water. The barrier is breathable which means that it transport vapor away from the body even though liquid water cannot pass through [15].

A coating is applied, often in viscous form, to the fabric and then cured [16]. A coating can be applied via dip coating, where the substrate is immersed in the coating liquid and then withdrawn. Another method is knife coating where the coating material is applied to the fabric and the coating thickness is directed by a metering blade [17]. A laminate is a pre-made film that is attached to the fabric [16]. It can be applied with, for example, adhesive lamination or flame lamination. In wet adhesive lamination, the adhesive is applied to a surface by a coating method. The coated substrate is then applied to another substrate under pressure. In flame lamination a thermoplastic foam sheet is passed over a flame and a thin molten polymer layer is formed. The molten layer is used as an adhesive between two substrates [17]. The surface of the fabric itself needs to be water and soil repellent. Otherwise the fabric would get saturated with water and the barrier would lose its breathability. This is done by a textile finishing process and it is this process that is in focus in this project.

Impregnated textiles lose their properties after repeated wear and washing [15]. There are standard methods to simulate aging of the fabrics, for evaluation of the durability of the impregnation. Martindale is a standard method used to simulate abrasion. The fabric is rubbed against a standard fabric for a number of cycles under a certain load. There are also standard methods for laundering. When impregnated with fluorocarbons the fabric needs to be dried at high temperatures after laundering in order to retain the hydrophobic/oleophobic properties [14].

2.4 Hydrophobicity and Oleophobicity

Hydrophobicity and oleophobicity is the ability of a surface to repel water and oil respectively. This ability is determined by both the surface roughness and the surface free energy. For a liquid to spread on a material it must have a surface energy lower than the surface free energy of that material [18]. To achieve a hydrophobic surface the surface free energy must therefore be lower than 72 mN/m, which is the surface tension of water. To achieve an oleophobic surface, the surface free energy must be even lower since most oils have a surface tension around 20-30 mN/m. Only fluorocarbons show a low enough surface energy to be used for this purpose [15].

2.4.1 SURFACE TENSION

Molecules located in the bulk and at the surface of a liquid experience different environments. In the bulk, the molecules experience the same attractive forces from all direction whilst at the surface there are different forces from different directions. The net attraction of the surface molecules will be towards the bulk which creates the surface tension. The shape of a liquid on a surface will adjust to minimize the total surface energy [6].

The extent of spreading of a liquid on a surface is dependent on the surface tensions of the liquid (γ_{LV}) and the solid (γ_{SV}) and the interfacial tension between solid and liquid (γ_{SL}). The forces acting on a drop at a surface are illustrated in figure 3.

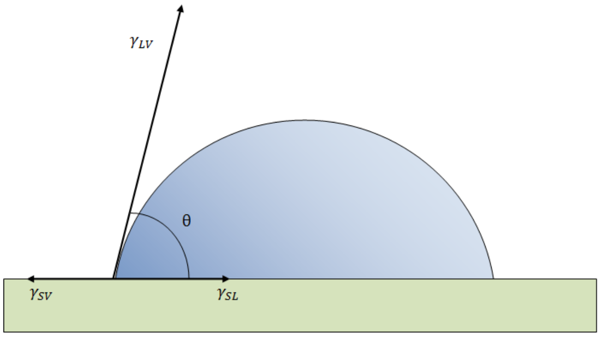

Figure 3: Shows the forces that are acting on a droplet in contact with a surface.

The interfacial tension between solid and liquid (γ_{LV}) and the horizontal component of the surface tension of the liquid ($\gamma_{LV}\cos\theta$) work in one direction and the surface free energy of the solid (γ_{SV}) work in the opposite direction. However, for contact angles above 90° the term $\gamma_{LV}\cos\theta$ will be negative. The equilibrium between a liquid drop and the surface is described by Young's equation [18]:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta \tag{2.1}$$

Young's equation only holds for ideal, smooth surfaces. Most surfaces are non-ideal and the contact angles measured on them are called apparent contact angles [19].

2.4.2 WETTING BEHAVIOR OF ROUGH SURFACES

Introducing surface roughness to a flat surface will increase the wetting/nonwetting behavior of the surface. Hence, a hydrophobic surface will be more hydrophobic and a hydrophilic surface will be more hydrophilic [15].

Robert N.Wenzel described in 1936 the situation where a water droplet fills the cavities in the rough surface, thereby making the actual surface/liquid interface larger than if the surface would have been smooth. For a hydrophobic surface this will lead to an increase in contact angle since the shape of the droplet becomes more spherical to reduce the contact between water and solid. The reverse is true for a hydrophilic surface. Thus, surface roughness will enhance the wetting behavior of a hydrophilic surface and the non-wetting behavior of a hydrophobic surface. Wenzel introduced the roughness factor to describe the relation between actual and geometric surface [20]:

$$r = \frac{actual\ surface}{geometric\ surface} \tag{2.2}$$

and the Wenzel model that describes homogeneous wetting according to the equation:

$$\cos\theta' = r\cos\theta \tag{2.3}$$

Where θ' and θ are the apparent contact angle and the Young contact angle respectively [21].

In 1944, Cassie and Baxter extended the Wenzel model to also be valid for porous surfaces. The Cassie-Baxter equation describes the situation when air is trapped in the cavities between the liquid and the surface.

$$\cos\theta' = f_1 \cos\theta - f_2 \tag{2.4}$$

Where f_1 and f_2 are the area of solid-liquid interface and liquid-vapor interface respectively, for a unit area. θ' is the apparent contact angle and θ is the Young contact angle. For a non-porous, rough surface f_2 is zero and the Cassie-Baxter equation simplifies to the Wenzel equation with roughness factor, f_1 [22]. Figure 4 shows the Wenzel and Cassie-Baxter states.

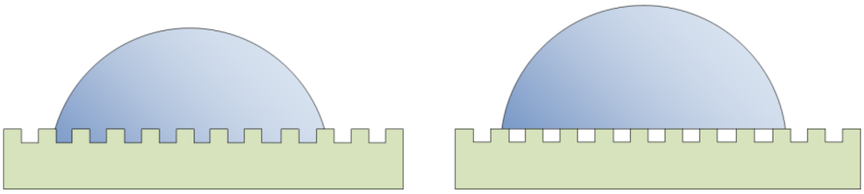

Figure 4: Illustration of the Wenzel (left) and Cassie-Baxter (right) states

Fabrics are different from perfectly smooth surfaces since they are not smooth and contain capillaries between, and in, the yarns. The time for a droplet to sink into the fabric depends both on the wetting behavior of the surface and on the shape and size of the capillaries of the fabric. The movement of the liquid into the fabric, due to capillary forces, is called wicking. Wicking can only occur if the liquid can wet the surface [6].

2.4.3 CONTACT ANGLE HYSTERESIS AND ROLL OF ANGLES

When roughness or chemical heterogeneity is introduced to a surface, it will show contact angle hysteresis; that is the difference between the advancing (largest) and receding (smallest) contact angles [18]. For a droplet at a tilting surface the advancing and receding contact angle can be obtained as can be seen in figure 5.

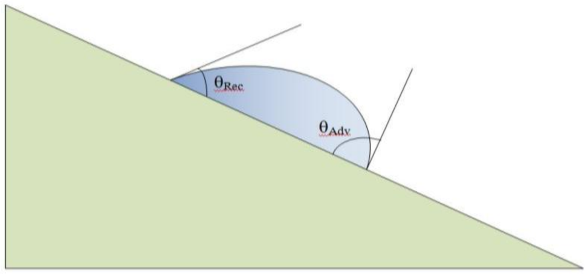

Figure 5: Shows a droplet on a tilted surface. The advancing and receding contact angle is the angles in the front and in the rear of the moving liquid.

For a droplet that has no contact angle hysteresis on a repellent surface the situation will look like figure 6. The droplet will easily roll-off at a low tilting angle.

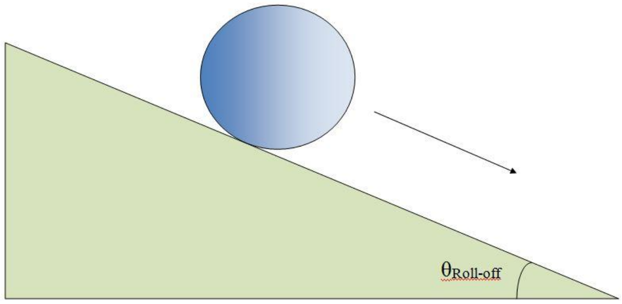

Figure 6: Illustration of the behavior of a water droplet on a superhydrophobic surface with no contact angle hysteresis. The angle at which the droplet starts to roll of the surface is called the roll-off angle.

A Cassie-Baxter drop shows less contact angle hysteresis and therefore lower roll-off angle than a Wenzel drop. When forming a superhydrophobic surface it is therefore important to design it such that a Cassie-Baxter drop is formed [23]. A superhydrophobic surface should have a water contact angle greater than 150° and a low roll-off angle. The mass of a water droplet has a strong influence on the roll-off angle why it is important to use the same drop volume for all measurements. Due to this it is hard to set a fixed value as requirement on the roll-off angle for a surface to be called superhydrophobic. However, a commonly used value is that the roll-off angle should be less than 5° [24].

2.5 Fluorocarbons

In a polyfluorinated compound most of the hydrogen atoms in the molecular structure are replaced by fluorine atoms, and if all hydrogen atoms are replaced the compound is called perfluorinated. Fluorinated compounds are used in a wide range of applications. They are for example used in firefighting foams since they are efficient for liquid fuel fires. Foams containing perfluorooctane sulfonate (PFOS) are no longer produced, except in China, but may still be used since they have a long shelf-life. They are instead substituted with shorter-chained fluorinated compounds. In the textile industry, fluorinated substances are used to give oil and water repellent finishes. Fluorinated compounds are also used in paper and packaging, for example to give oil repellency to food-contact papers.

The first perfluorinated compound that gained attention for its toxicity and widespread occurrence in the environment was PFOS and this substance is now restricted. The second substance to attract concern was Perfluorooctanoic acid (PFOA) [3]. Both PFOS and PFOA are perfluoroalkyl acids (PFAAs) and derivatives of them, that are used industrially, will degrade or metabolize to the corresponding PFAA as an end-product [25]. PFOS is a type of perfluoroalkyl sulfonate (PFSA) and PFOA is a perfluoroalkyl carboxylate (PFCA), both PFOS and PFOA are examples of fluorinated surfactants with a chain length of 8 carbons. A fluorinated surfactant consists of a fluorinated tail and a hydrophilic head. The two groups are connected with an organic group, called a spacer. The hydrophilic head can be nonionic, anionic, cationic or amphoteric, which means it can react as both an acid and a base. Polyfluorinated compounds have been produced synthetically for 50 years and do not occur naturally.

There are studies that indicate that even the short chain length fluorocarbons have toxic effects on the environment and human health, although these substances are considered to be less harmful than the ones of longer chain length. There is need for more environmental studies on these compounds. PFOA and PFOS have been found in the arctic, far from any source, which means that these substances are global contaminants. Since 2010 the levels of PFOA and PFOS in the environment have decreased while the levels of short-chained sulfonates have increased.

Exposure to humans of perfluorinated compounds occurs mainly via food, drink and indoor dust. Fluorocarbons accumulate in internal organs and blood since they bind to proteins in cell membranes and serum proteins. PFAAs have been found in human blood all over the world. Especially PFOS and PFOA have been detected frequently. The chemicals have also been detected in human breast milk, but the levels have been lower than in blood.

PFCAs and PFSAs have been shown to have a negative effect on reproduction, development and immune system. Short-chained PFAAs are less toxic during the developing stages than the longer-chained. This is partly due to that they leave the body at a faster rate. Some reports have shown that there is a potential relationship between the exposure to PFOS and PFOA and the risk of being diagnosed with ADHD. However, further studies are required on the subject. There are also studies that come to different conclusions about the toxicity effect of these chemicals and therefore further research is needed.

In 2008 a restriction of the use of PFOS in fabrics was introduced within EU legislation. C6-chemistry has come to replace the previously used C8-chemistry [3].

2.6 Non-fluorinated hydrophobizing agents

There are a number of non-fluorinated alternatives that can render hydrophobic surfaces but they will not give any oleophobicity, since their surface energies are not low enough. The first materials to be used as water repellents were probably hydrocarbon based, like wax and oils. In the 1950's silicone-based materials was introduced as water repellents. One common silicon based water repellent is PDMS (Poly(dimethylsiloxane)). It consists of a siloxane skeleton with methyl groups and creates a closely packed hydrocarbon surface [26].

2.6.1 DENDRIMERS

Dendrimers are highly branched molecules; they consist of a number of branched organic units attached to a core molecule. Dendrimers can carry functional groups and may be used in a wide variety of applications, such as drug delivery or as contrast agents for magnetic resonance imaging. [27]. Dendrimers can be used to give the surface a nanostructure that might increase the hydrophobic behavior, as discussed in section 2.4.2 [28]. Examples of different dendrimer structures are illustrated in figure 7.

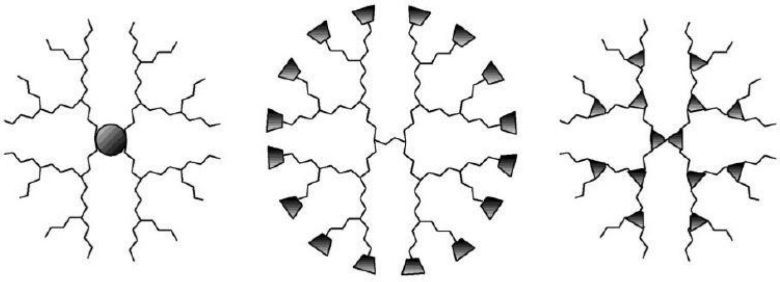

Figure 7: Examples of dendrimers with different locations for the functional groups, reprinted from [27].

2.7 Wet chemical treatment

Wet chemical treatment is the conventional method for impregnating fabrics. It is cost-effective for production in large quantities [15]. The fabric is treated with the chemicals through a dipping process. The fabric is then passed through a foulard, which means that it is squeezed between two rollers to remove the excess liquid [29]. The pressure between the rollers should be specified to ensure a certain and constant uptake of the chemical solution, called 'pick-up'.

$$Pick-up\ \% = \frac{Rolled\ weight\ of\ fabric - Dry\ weight\ of\ fabric}{Dry\ weight\ of\ fabric} \tag{2.5}$$

After the fabric has passed through the foulard it needs to be dried and cured. Wet chemical treatment is a method that consumes a lot of water and chemicals and it is therefore not environmentally friendly [4]. The set-up for the wet chemical treatment is illustrated in figure 8.

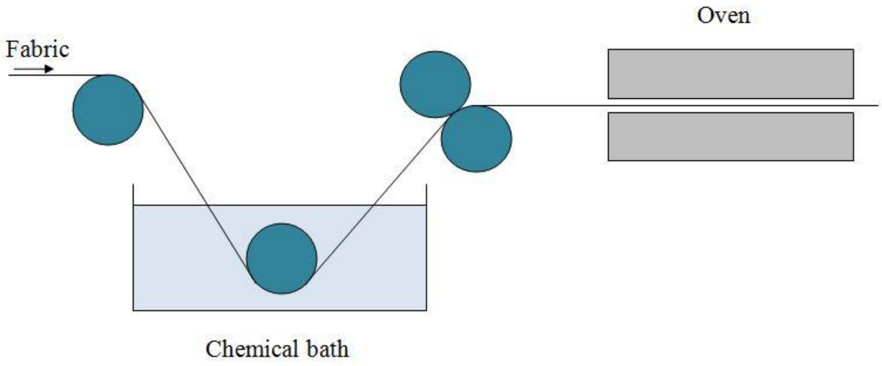

Figure 8: Illustration of the wet chemical treatment set-up.

2.8 Plasma

Langmuir first described the plasma phenomenon in 1929 [30]. Plasma is ionized gas and is sometimes called the fourth state of matter since it has unique chemical and physical properties that differ from solids, liquids and gases [31]. It consists of a mixture of electrons, ions, radicals, excited neutral atoms and UV-radiation [6]. It is an estimation that over 99% of the apparent universe consists of plasma. One example of naturally occurring plasma is the lightning that is developed during thunderstorms [32]. Another is the Aurora Borealis (Northern lights) [33]. When a voltage is applied to a gas, the gas will break-down and start to conduct electricity since the atoms and molecules in the gas gets ionized. The motion of the particles in a plasma field can create charge concentrations that generate long-range coulombic fields that affect charged particles at a long distance. This gives the plasma a collective behavior [34]. The positive and negative charges in the plasma act collectively since the coulomb forces between the charges dominate over externally applied forces [31].

There are two different kinds of plasma; non-thermal and thermal plasmas. In non-thermal plasma, the ions and the neutral atoms and molecules stay at room temperature while the electron temperature is much higher [31, 35, 32]. Since the electrons constitute much less than a millionth of the total mass, their temperature is negligible and thus the plasma has an overall low temperature. The electrons collide with other constituents of the plasma generating a lot of different, highly energetic species which will bombard and modify the surface of a material present in the plasma [35]. Non-thermal plasmas are suitable for the treatment of fabrics since reactions can be initiated without heat, which could destroy the fabric. It is also a versatile technique that makes it possible to modify the fabric with a wide variety of functional groups, such as carboxyl and hydroxyl groups [36]. Non-thermal plasmas are sometimes referred to as cold plasmas. With higher gas density, the collisions between the electrons and heavy particles become more frequent and all the constituents reach the same temperature [31]. If all the different constituents in the plasma have similar temperatures the plasma is hot and is called thermal plasma. Thermal plasma can for instance be used in metallurgy and welding but is not suitable for the textile industry [35].

2.8.1 *ATMOSPHERIC PRESSURE PLASMA*

It is harder to generate large volume plasmas at atmospheric pressure than at reduced pressure. When the pressure rises, the gap between the electrodes must be smaller to generate plasma, if the voltage is fixed. It is easier to control the gas atmosphere in vacuum plasma than in atmospheric plasma equipment, which is open to the surrounding environment; on the other hand, atmospheric plasma is compatible with the continuous processing in textile industry, which is an advantage [35]. Atmospheric plasma also makes it possible to get shorter process times and it requires less energy than vacuum plasma [37].

2.8.1.1 Dielectric barrier discharge

The Dielectric barrier discharge is used to produce non-thermal plasma at atmospheric pressure [38, 39]. It consists of two electrodes with a gap in between of a few millimeters. A high voltage is applied over the electrodes, which makes the gas break down and a plasma discharge is generated [35]. At least one of the electrodes is covered with an insulating material which acts as a dielectric barrier for electric currents [38]. This prevents uncontrolled currents like the formation of arcs and the plasma is forced to spread out over the whole electrode area [35]. Since the electrodes are quite large (ca 0.1 m^2) while the gap between them are in the millimeter range the DBD has a large surface-to-volume ratio, which helps maintaining the low gas temperature. Due to the small gap between the electrodes, large and complex samples cannot be treated in the DBD, but it is appropriate for fabrics and other flat samples [32]. It is also suitable for in-line production since the fabrics can be treated from roll to roll.

2.8.2 *PLASMA TREATMENT OF TEXTILE MATERIALS*

Research on plasma treatment of textiles started in the early 1980s [40]. In many cases it is the surface properties of fabrics that determine their use. Cold plasma treatment can be used to modify the surface of textile materials without altering the bulk characteristics, which is affected when traditional wet finishing is performed [4, 33]. Another advantage with plasma is that it can be used to treat all kinds of textiles, even delicate ones [4]. There are a number of characteristics of a fabric that can be altered using plasma treatment; it can be used to enhance dyeability and adhesion and to change the hydrophobicity and oleophobicity of the surface [32].

Ceria and Hauser performed atmospheric plasma treatment on acrylic fabrics, followed by a wet chemical treatment with a fluorocarbon-containing chemical. The durability of the impregnation was tested. The fabrics were washed repeatedly and water and oil repellency was tested before and after washing. They showed that the plasma treatment improved the durability of the impregnation after ageing [41]. Ramamoorthy et al performed plasma induced graft polymerization of fluorocarbons onto cotton fabrics. They achieved a nanolayer of fluorocarbons that was resistant to five home launderings [42]. Leroux et al deposited a fluorocarbon coating on polyester by injecting a fluoropolymer into the plasma. They showed that the plasma treatment increased the adhesion of the fluoropolymer to the fabric [43].

Plasma can be used to alter the surface in a number of ways including creation of reactive sites, etching or cleaning, and grafting of functional groups. To clean or etch a surface an inert gas is used. When the surface is bombarded, covalent bonds are broken, which leads to the detachment of contaminants. Plasma treatment can also be used to activate the surface by the formation of reactive sites. The surface can then form covalent bonds with substances that can render the surface desired properties. Chemicals can also be directly grafted onto the surface if they are present in the plasma. They will form radical species that will react with the surface. The molecules can also react with themselves and thus forming a polymeric layer on the surface, this is called polymerization [4].

Plasma treatment is more environmentally benign than conventional wet chemical treatment. It is a dry process and, being a surface-specific technique, the consumption of chemicals and energy is much lower than when wet processing is used [4, 33]. In this project a wet chemical treatment is combined with the plasma treatment making the environmental winnings less than if, for instance, a spraying process would have been used. However, the amount of chemicals can be reduced if the coupling between chemicals and fabric is strengthened. It would also mean that the amount of chemicals released in the environment would be lowered.

3. METHOD

In this section the materials and chemicals used in the thesis work will be described. Further, the methods used will be explained.

3.1 Material

The fabric used in this project was a polyamide. An industrially impregnated sample, of the same fabric, with a laminated inside was used as a reference. Both fabrics were delivered from FOV fabrics. The properties of the fabric are listed in table 1.

Table 1: Properties of the polyamide fabric used in the study

Construction	100% Polyamide
Weave	Plain weave
Weight	100 g/m^2
Number of threads per centimeter	Warp: 47 Weft: 28
Number of filaments per thread	Warp: 23 Weft: 68
Tex	Warp: 78 Weft: 190

The unit Tex is used to describe the fineness of a fiber or thread. It is the weight in grams of 1000 meters of the thread/fiber [7].

3.2 Chemicals

The chemical used for impregnation of the fabrics was a C6-based fluorocarbon; ®RUCO-GUARD AFB6 CONC. ®RUCO-DRY ECO, a fluorocarbon-free dendrimer-based finish, was also used in combination with the fluorocarbon. The polymers in ®RUCO-DRY ECO are larger than 100 nm. The chemicals were provided by Rudolf Chemie.

3.3 Wet chemical process

The samples were immersed in the chemical solution and squeezed one time in a foulard to remove the excess liquid. A pressure of 5.0 bar and a speed of 1.7 m/min were used. The samples were then dried at 120 degrees Celsius for 70 seconds. After this they were cured for 1 min at 160 degrees Celsius. This was performed according to recommendation by Rudolf Chemie and in line with a typical commercial finishing process.

3.4 Plasma

The plasma equipment used in this study was a PLATEX 600 LAB dielectric barrier discharge (DBD) plasma, made by GRINP, Italy. An illustration of the plasma equipment can be seen in figure 9.

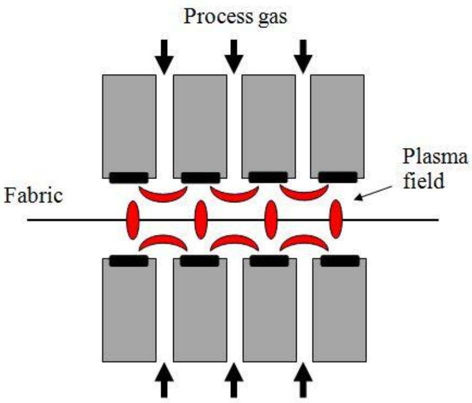

Figure 9: Illustration of the dielectric barrier discharge plasma.

The optimal parameters for the plasma treatment should be determined. The fabric was plasma treated with different types and amounts of gases along with different power settings and treatment times. After the optimal parameters were found different concentrations of the hydrophobization agents were evaluated.

The plasma processing parameters that were constant for all treatments are listed in table 2.

Table 2: Constant plasma treatment parameters

Plasma parameter	Value
Speed of frame	0.04 m/s (setting 1.6)
Electrode temperature	30°C
Distance between the electrodes	3.0 mm

3.5 Ageing of samples

For evaluation of the resistance to ageing the samples were exposed to laundering and Martindale abrasion.

3.5.1 LAUNDERING

The samples were washed repeatedly according essentially to standard SS-EN ISO 6330:2012. The washing procedure used was 4N (40 degrees Celsius) and the detergent used was ECE-A with a dosage of 20 g per washing cycle. 100 % polyester loading fabric (EN-ISO 26330:1994) was used so that the total weight was 2 kg. After each wash the samples were tumble dried for 30 minutes at maximum temperature of 80 degrees Celsius. The tumble dryer used was an Electrolux T3650.

3.5.2 MARTINDALE ABRASION

The abrasion resistance of the samples was evaluated using the Martindale procedure according essentially to the standard SS-EN ISO 12947-2. The samples were rubbed against a standard wool fabric for 5000 cycles at a load of 12 kPa. The oil and water repellency was measured before and after Martindale abrasion.

3.6 Spray test

The water repellency of the treated fabrics was evaluated according essentially to the standard test SS EN 24 920. 100 ml of distilled water was sprayed onto the surface and the samples were examined visually and graded according to the standard ISO below. Half grades were used when needed.

ISO 0 –Wetting of both sides of sprayed sample surface, complete wetting
ISO 1 – Wetting of sprayed side of the fabric
ISO 2 – Partial wetting of sprayed surface
ISO 3 – Wetting of sprayed surface at sprayed spots
ISO 4 – Small wetting or sticking of droplets
ISO 5 – No wetting or adherence of droplets

Before the spray test all samples were stored a minimum of 4 hours in controlled climate with a temperature of 20±2 degrees Celsius and a relative humidity of 65±4%.

3.7 Oil repellency test

The oleophobic behavior of the treated samples was studied according essentially to the standard oil repellency test SS-EN ISO 14419:2010. Eight oils with decreasing surface tension were used; the compositions can be seen in table 3.

Table 3: Compostition of test liquids for the oil repellency test

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-dodecane	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

The samples got an oil repellency grade which corresponded to the highest number of test liquid that did not wet the surface. Five drops of the oil were placed with a pipette at the surface and examined visually from about 45 degrees after 30 seconds. The spreading of the drop was compared to descriptions and pictures from the standard test. Three of the five drops must not wet the surface for the sample to pass the test. Before the oil repellency test, all samples were stored a minimum of 4 hours in controlled climate with a temperature of 20±2 degrees Celsius and a relative humidity of 65±4%..

3.9 Contact angle measurements

Contact angles were measured with the sessile drop technique. Droplets of deionized water were dropped from a height of 6 mm above the sample and it was video recorded for 30 seconds. The contact angles at the beginning and after 30 seconds were evaluated. For each sample, three fabrics were tested with two drops on each fabric; 6 drops in total were evaluated. The volume of the droplets was set to 11 µl. A DSA30E instrument from Krüss GmbH, Germany was used to perform the measurements.

3.10 Soil repellency

To evaluate the soil repellency of the fabrics coffee, orange juice and milk chocolate was used as soil substances. The amounts used of each substance can be seen in table 4.

Table 4: Amounts of substances used for the stain repellency test

Substance	Amount
Coffee	0.5 ml
Orange Juice	0.5 ml
Chocolate	0.5 g

The substances were placed on the fabrics and allowed to dry overnight. For each substance three samples were made. The substances were first removed mechanically and then the stains were stroked five times with a wetted paper tissue. The remaining stains were evaluated by comparison between the different samples.

4. RESULTS AND DISCUSSION

In this section the results from the experiments performed in the study are presented and discussed. In table 5 all the plasma treated samples are presented along with the three reference samples. For samples 1-14, which were used for screening to determine the optimal plasma parameters, one piece of fabric were treated and evaluated. However, there was enough material to evaluate the oil repellency and contact angles for different areas of the fabric. Of the other samples triplets were made for the evaluation. Unless otherwise stated, the differences between the triplets have not been larger than 0.5 units for the water and oil repellency tests.

Table 5: Shows the plasma treatment parameters and concentrations of hydrophobizing agents for the different samples that were prepared in the study.

Sample	Fluorocarbon concentration (g/l)	Dendrimer concentration (g/l)	Gas flow (l/minute)	Power (W)	Treatment time (s)
1	30	0	He: 5	600	8
2	30	0	He:5, O_2: 0.2	600	8
3	30	0	He:5, N_2: 0.2	600	8
4	30	0	He:5, O_2: 0.5	600	8
5	30	0	He:5, N_2: 0.5	600	8
6	10	0	He: 5	400	4
7	10	0	He: 5	400	8
8	10	0	He: 5	400	16
9	10	0	He: 5	600	4
10	10	0	He: 5	600	8
11	10	0	He: 5	600	16
12	10	0	He: 5	800	4
13	10	0	He: 5	800	8
14	10	0	He: 5	800	16
15	5	0	He: 5	600	8
16	5	25	He: 5	600	8
17	30	0	-	-	-
18	10	0	-	-	-
19	0	30	-	-	-

The treatment time was calculated according to equation 4.1. The length of the electrodes and the speed of the frame were constant but the number of treatments cycles varied for different samples in this study.

$$Treatment\ time\ (t) = \frac{Length\ of\ the\ electrodes * Number\ of\ treatment\ cycles}{Speed\ of\ frame} \tag{4.1}$$

A water and oil repellent fabric of commercial grade, produced by FOV was used as a reference and is called sample 20.

4.2 Plasma treatment

In this section the results from optimizing the plasma treatment parameters are presented and discussed. Kan and Yuen showed that atmospheric plasma treatment of polyamide gave a better result as a pre-treatment than it did as post-treatment [44]. Due to this, and the fact that plasma post-treatment might give potentially toxic by-products from the impregnation chemicals, plasma pre-treatment was used in this study.

4.2.1 CHOICE OF REACTIVE GAS

To specify the parameters that should be used for the plasma treatment the following procedure was conducted. First the reactive gas to be used was chosen. The gas flow was varied according to table 6.

Table 6: Gas flow during plasma treatment for sample 1-5.

Sample	Gas flow (l/minute)
1	He: 5
2	He: 5, O_2: 0.2
3	He: 5, N_2: 0.2
4	He: 5, O_2: 0.5
5	He: 5, N_2: 0.5

The samples were treated at a power of 600W for 8 s (2 cycles in the plasma zone). After treatment the samples was evaluated with spray test and oil repellency test and the gas composition showing the best result was chosen for further evaluation. The results are presented in table 7.

Table 7: Oil and water repellency of samples plasma- treated with different gas compositions.

Sample	Oil repellency grade	Water repellency grade
1	6	ISO 5
2	6.5	ISO 5
3	6	ISO 4
4	6	ISO 5
5	6	ISO 5

As can be seen in table 7 the results for the different gas compositions were very similar. The water repellency was high for all the samples. Sample 3 showed small adherence of droplets and was graded as ISO 4. The other samples showed no adherence at all. When there is no adherence of drops the droplets are probably in the Cassie-Baxter state. The increased drop adherence is an indication that the droplets moves to the Wenzel state, with wetting of the cavities in the surface. The oil repellency was similar for all the samples.

To evaluate the difference in durability between the samples, all samples were washed repeatedly and the water repellency was tested using the spray test. The results from the spray test can be seen in table 8.

Table 8: Water repellency, before and after repeated laundering, of samples plasma- treated with different gas compositions.

Sample	Before laundering	after 1 cycle	After 5 cycles	After 10 cycles	After 15 cycles	After 20 cycles
1	ISO 5	ISO 4	ISO 4	ISO 4	ISO 4	ISO 4
2	ISO 5	ISO 4	ISO 4	ISO 4	ISO 4	ISO 3.5
3	ISO 4	ISO 4	ISO 4	ISO 4	ISO 4	ISO 3.5
4	ISO 5	ISO 4	ISO 4	ISO 4	ISO 4	ISO 4
5	ISO 5	ISO 4	ISO 4	ISO 4	ISO 4	ISO 4

As can be seen in table 8, sample 3 obtained the same water repellency grade after 1 cycle of laundering as before. However, an increase in the adherence of drops could be seen. After 1 cycle all the samples got the same water repellency grade. After 5 times of repeated washing, all samples showed an increase in the drop adherence though the grade was still the same. Since no major differences between the samples could be seen they were further washed.

After 15 cycles of washing some differences could be seen between the samples even though they obtained the same grade. Sample 3 showed the largest adherence of drops while sample 1 showed the lowest adherence. After 20 cycles of laundering sample 2 and 3 obtained a lower repellency grade than the other samples.

The oil repellency of the samples was tested after 15 cycles and the result can be seen in table 9.

Table 9: Oil repellency, before and after 15 cycles of repeated laundering, for samples plasma- treated with different gas compositions.

Sample	Oil repellency before laundering	Oil repellency after 15 cycles
1	6	5
2	6.5	5.5
3	6	5
4	6	5
5	6	5

It can be seen from table 9 that the oil repellency was very similar for all the samples. Sample 2 got half a grade higher than the other samples. However, the differences are very small.

The abrasion resistance of the samples was further investigated using the Martindale procedure. The water and oil repellency was measured after the abrasion. After the abrasion all the samples got a water repellency grade of ISO1 and an oil repellency of 4. It could be concluded that a less aggressive abrasion should have been conducted in order to see at which state the different samples started to lose their water repellency. That could have shown clearer differences between the samples, and more conclusions could have been drawn. Although the differences between the samples were small, pure helium was chosen to be the gas to be used in forthcoming plasma treatments, since sample 1showed the best water repellency and good oil repellency. Additionally, that was the alternative that gave the lowest gas consumption.

4.2.2 CHOICE OF PLASMA PARAMETERS

One aim of the project was to lower the fluorocarbon concentration. The concentration was lowered already during the determination of the plasma parameters since the samples needed to be laundered 20 times before significant differences could be seen between them. The fluorocarbon concentration was lowered to 10 g/l for further plasma treatment to achieve a faster evaluation.

In order to choose the plasma parameters, 9 samples were treated with varied power and treatment time as can be seen in table 10.

Table 10: Power and treatment times for sample 6-14.

Sample	Power (W)	Treatment Time (s)
6	400	4
7	400	8
8	400	16
9	600	4
10	600	8
11	600	16
12	800	4
13	800	8
14	800	16

The helium gas flow was kept constant at 5 liters/minute. The samples were studied with oil repellency test and spray test, both before and after repeated laundering. The results of the water repellency test can be seen in table 11.

Table 11: Water repellency of the nine samples treated with different treatment power during varying treatment times, before and after repeated laundering.

Sample	Before laundering	After 1 cycle	After 5 cycles	After 10 cycles	After 15 cycles
6	ISO 4	ISO 4	ISO 4	ISO 3	ISO 2.5
7	ISO 5	ISO 4	ISO 4	ISO 4	ISO 3.5
8	ISO 5	ISO 4	ISO 4	ISO 4	ISO 3
9	ISO 5	ISO 4	ISO 4	ISO 4	ISO 3.5
10	ISO 5	ISO 4	ISO 4	ISO 4	ISO 3.5
11	ISO 5	ISO 4	ISO 4	ISO 3	ISO 3
12	ISO 5	ISO 4	ISO 4	ISO 4	ISO 3.5
13	ISO 4	ISO 4	ISO 4	ISO 3	ISO 3
14	ISO 5	ISO 4	ISO 4	ISO 4	ISO 3.5

After 1 cycle of laundering, all the samples got the grade ISO 4, as can be seen in table 11, even though there were some differences between them. All the samples that had a water repellency of ISO 5 before laundering showed a minor adherence of droplets, while the others showed a bit more adherence. It is notable that sample 13 showed lower water repellency than sample 12 and 14. One explanation could be that the whole sample was not impregnated properly. It could be seen that there were more adherence of drops at one side of the sample than on the other side. After 5 cycles all the samples still had a water repellency of ISO 4. ISO 4 is a quite broad grade since it goes from small adherence of droplets to partial wetting. After 10 laundry cycles sample 6, 11 and 13 obtained lower grades than the other samples. After 15 cycles of repeated washing sample 7, 9, 10, 12 and 14 obtained the highest grade of all the samples. Of these, sample 10 and 14 were the once that showed least wetting.

The oil repellency of the samples before laundering and after 10 and 15 cycles are presented in table 12.

Table 12: Oil repellency of the nine samples treated with different treatment power during varying treatment times, before and after repeated laundering.

Sample	Before laundering	After 10 cycles	After 15 cycles
6	6	4	4
7	6	5	5
8	6	5	4
9	6	5	5
10	6	5	5
11	6	5	5
12	6	5	5
13	6	4	5
14	6	5	3

As stated above, sample 10 and 14 showed the best water repellency after 15 laundry cycles. However, as can be seen in table 12, sample 10 clearly had a better oil repellency than sample 14 after 15 laundry cycles. Hence, the treatment time and treatment power was set to 8 s and 600 W for the forthcoming experiments. It can be seen that sample 13 got a higher oil repellency grade after 15 washes than after 10 washes; this might be due to uneven application of chemicals. A tendency of this could also be seen from the spray test, where one side of the sample showed more wetting than the other. Since the wet chemical treatment was conducted in the same way for all treatments the unevenness of the impregnation is probably connected to the plasma treatment. Both sample 13 and 14 showed some inconsistency in the repellency behavior indicating that the plasma dosage was too high, leading to increased etching of the surface [36]. Activated sites may have been removed leading to a lower degree of reaction between surface and fluorocarbons.

4.1 Reference sample

Samples were prepared conventionally with different concentrations to be used as references. A water and oil repellent fabric of commercial grade, produced by FOV was also used as a reference. The water repellency of the references was evaluated before and after repeated laundering and the results can be seen in table 13.

Table 13: Water repellency of the conventionally treated samples prepared in this study (Sample 17, 18 and 19) and of the industrial reference (sample 20). Sample 17 and 18 were treated with a FC-dispersion with a concentration of 30 g/l and 10 g/l respectively. Sample 19 was treated with a dendrimer-dispersion with a concentration of 30 g/l. Water repellency was measured before and after repeated laundering.

Sample	Before laundering	After 1 cycle	After 5 cycles	After 10 cycles	After 15 cycles	After 20 cycles
17	ISO 5	ISO 4	ISO 4	ISO 4	ISO 3	ISO 2.5
18	ISO 4	ISO 4	ISO 3.5	ISO 2	ISO 1.5	-
19	ISO 4	-	-	-	-	-
20	ISO 5	ISO 5	ISO 4.5	ISO 4	ISO 4	-

As can be seen in table 13, sample 19 was not evaluated after laundering. This was because that sample was only used to evaluate the effect of the pure dendrimer without aging. Sample 17 showed a hint of drop adherence but since it was hardly detectable it obtained a water repellency grade of 5. Samples 18 and 19 showed a clearer drop adherence.

The oil repellency of the reference samples were evaluated before laundering and after 15 cycles of repeated washing. The results from the oil repellency test are presented in table 14.

Table 14: Results of the oil repellency for the conventionally treated samples prepared in this study and for the industrial reference. The water repellency was measured before and after 15 cycles of repeated laundering.

Sample	Before laundering	After 15 cycles
17	6	5
18	6	3.5
19	0	-
20	6	5

As can be seen in table 14, sample 19 had no oil repellency before laundering; hence the oil repellency was not evaluated after laundering. When comparing sample 17 and 18 it can be concluded that a decrease in fluorocarbon concentration has a negative effect on the oleophobic behavior after 15 laundry cycles.

The plasma treated samples were compared to the industrially impregnated reference, but since all process parameters of that fabric was not known they were first of all compared to the conventionally treated samples, produced within this project. Table 14 shows that sample 17 and 20 are equal in oil repellency but according to table 13 the water repellency are slightly higher for sample 20.

4.3 Plasma treatment compared to conventional treatment

The plasma treated samples were compared to conventionally treated samples in order to evaluate the effect of the plasma treatment. The comparison of the water repellency for a fluorocarbon concentration of 30 g/l can be seen in the figure 10. The only difference between sample 1 and sample 17 is that sample 1 was pre-treated with plasma.

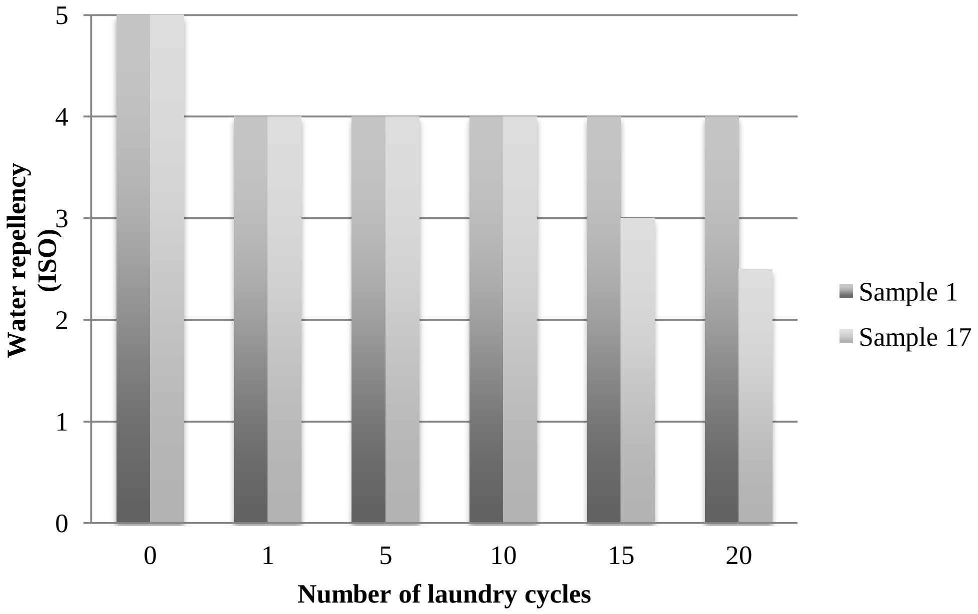

Figure 10: Water repellency of a plasma treated sample (sample 1) and a conventionally treated sample (sample 17). Both were treated with a FC-dispersion with concentration of 30 g/l. The water repellency was evaluated both before laundering and after repeated washing.

In figure 10 sample 1 is compared to sample 17. A difference between the samples can be seen after 15 laundry cycles where sample 1 obtained higher water repellency grades than sample 17. Sample 1 was only evaluated once in the spray test but sample 2-4 gave similar results. It can also be seen, when comparing with table 6, that even sample 2 and 3, which gave the lowest water repellency of the samples with different gas compositions, had higher water repellency than sample 17. It can therefore be concluded that the plasma treatment has a positive effect on the washing durability.

Figure 11 shows the comparison of the water repellency for a fluorocarbon concentration of 10 g/l. The only difference between sample 10 and sample 18 is that sample 10 was pre-treated with plasma.

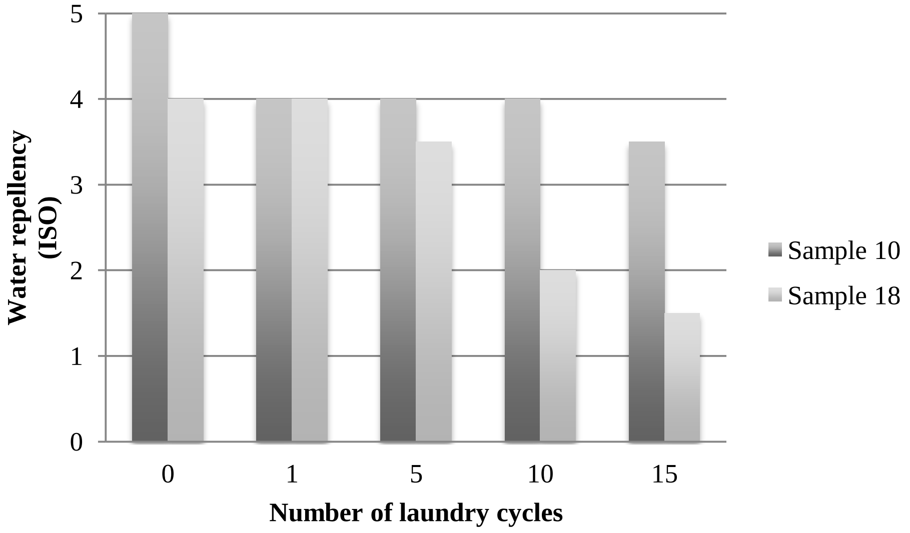

Figure 11: Water repellency of a plasma treated sample (sample 10) and a conventionally treated sample (sample 18). Both were treated with a FC-dispersion with concentration of 10 g/l. The water repellency was evaluated both before laundering and after repeated washing.

In figure 11 the differences in water repellency are even clearer than they were in figure 10. Sample 10 obtains higher water repellency grades than sample 18. Sample 10 was only evaluated once but as can be seen in table 11 and 12 samples 7, 9 and 12 obtained the same grades in both water and oil repellency. Since all plasma treated samples obtain higher repellency grades than sample 18, after repeated laundering, it contributes to the conclusion that the plasma treatment has a positive effect on the washing durability of the fluorocarbon finish. It can also be seen, when comparing figure 10 and 11, that sample 10 has the same repellency effect after 10 cycles of laundering as sample 17, and even higher after further washing. This is a clear indication that plasma treatment can be used to reduce the amount of chemicals needed to maintain the water repellency effect.

Since a fluorocarbon concentration of 10 g/l showed good results, the concentration was lowered even further. A FC-concentration of 5g/l was used. The repellency was measured as before and the results can be seen in figure 12, where the samples are compared to samples conventionally treated with a FC-concentration of 10 g/l. No sample conventionally treated with a FC-concentration of 5 g/l was evaluated, since the water repellency was poor at 10 g/l already.

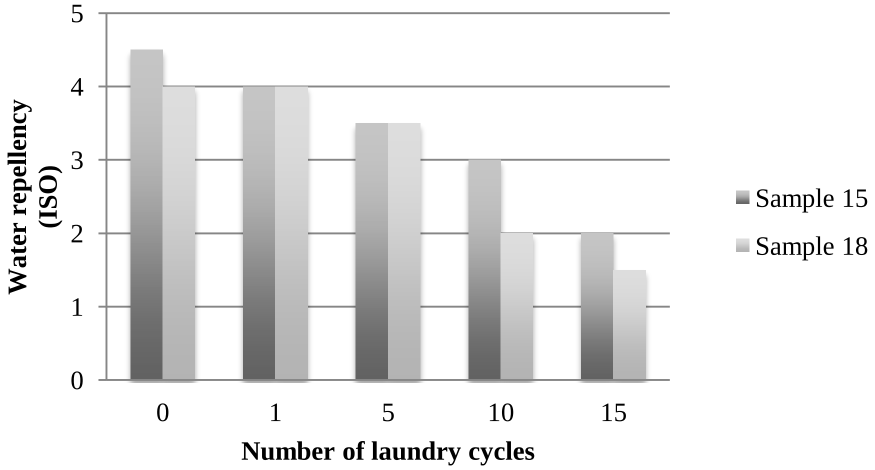

Figure 12: Water repellency of samples plasma treated with a concentration of 5g/l (sample 15) compared to samples treated conventionally with a concentration of 10g/l (sample 18). The water repellency was evaluated both before laundering and after repeated washing.

It can be seen from figure 12 that sample 15 are comparable in washing resistance, after 5 cycles, to sample 18. However, after 10 laundry cycles, sample 18 obtains a lower water repellency than sample 15. This contributes to the conclusion that plasma treatment makes it possible to reduce the fluorocarbon concentration. Another observation that can be made, when comparing figure 10, 11 and 12, is that the repellency behavior of sample 15 decreased faster than for the samples treated with higher fluorocarbon concentrations.

The oil repellency for samples 1, 10, 15, 17, 18 and 20, before and after 15 cycles of laundering, can be seen in figure 13.

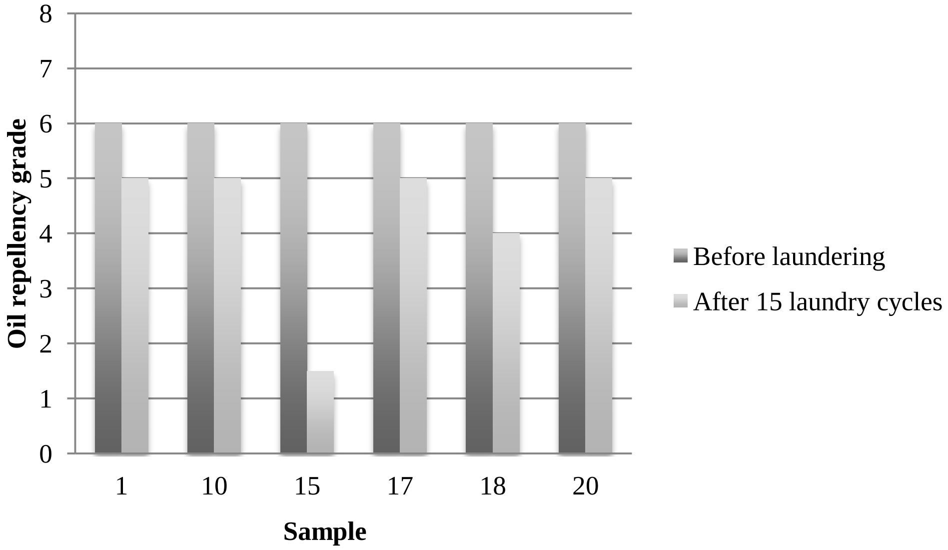

Figure 13: Oil repellency before laundering and after 15 cycles of laundering for both conventionally treated samples (17, 18, and 20) and plasma treated samples (1, 10 and 15).

As can be seen in figure 13 all the samples got obtained the same oil repellency grade before laundering. It can be seen that all samples have lost some of their oil repellency after 15 laundry cycles. Without plasma treatment the oil repellency goes down when the fluorocarbon concentration is lowered from 30 g/l to 10 g/l. The oil repellency after 15 laundry cycles decreased from 5 for the higher concentration to 4 for the lower concentration. For the plasma treated samples there was no difference in the oil repellency when the fluorocarbon concentration was lowered from 30 g/l to 10 g/l. This is in line with the observations from the spray tests, which gave that the washing durability of the plasma treated samples is better than that of the conventionally treated samples, indicating that the plasma treatment enhances the washing fastness of the impregnation.

To lower the fluorocarbon concentration to 5 g/l had a significantly negative effect on the durability of the finishing. Even though those samples showed good oleophobicity before laundering, they obtained an oil repellency grade as low as 1.5 after 15 cycles. It is worth noticing that three of the samples prepared in this study (sample 1, 10 and 17) obtained the same oil repellency grade as the industrial reference after 15 washes. Another observation to be made is that lowering the concentration of fluorocarbon from 30 g/l to 10 g/l seems to have a stronger negative influence on the water repellency than on the oil repellency.

4.4 Combination of fluorocarbon and dendrimer

A combination of fluorocarbon and dendrimer was evaluated in order to investigate if it could give any synergetic effects that would enhance the hydrophobicity and oleophobicity without increasing the amount of fluorinated chemicals. Dendrimers can change the structure of the surface, which might have a positive influence on the repellency.

A combination of fluorocarbon and dendrimer, 5g/l and 25 g/l respectively, was used. The two chemicals were mixed together before application to the plasma-treated textile. The washing resistance was evaluated as before. The results can be seen in figure 14 together with the results for the samples treated with a fluorocarbon concentration of 5g/l.

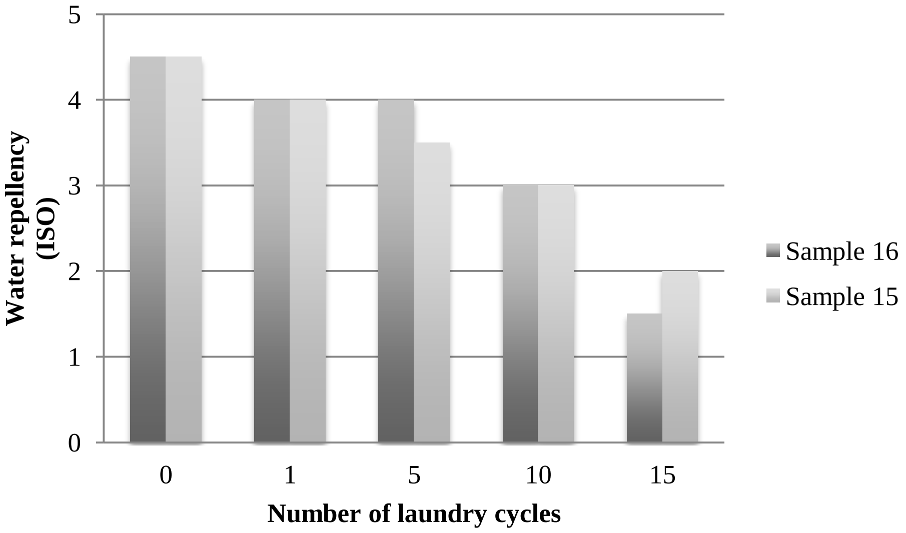

Figure 14: Water repellency of the samples treated with a mixture of FC and dendrimer, 5 g/l and 25 g/l respectively (sample 16) compared to the water repellency of plasma treated samples with a FC-concentration of 5g/l (sample 15).

The triplets of sample 15 showed differing results after 5 washes. One of the samples showed ISO 4 while another had a clear ISO 3. Hence, the grade was set to ISO 3.5. For sample 16, after 15 washes the water repellency grade was ISO 1 for one test and ISO 2 for the two others. For sample 15 the triplets showed a more consistent behavior; one got ISO 1.5 and the others ISO 2.

The oil repellency of sample 16, before and after 15 cycles of laundering are compared with the oil repellency for sample 15 in figure 15.

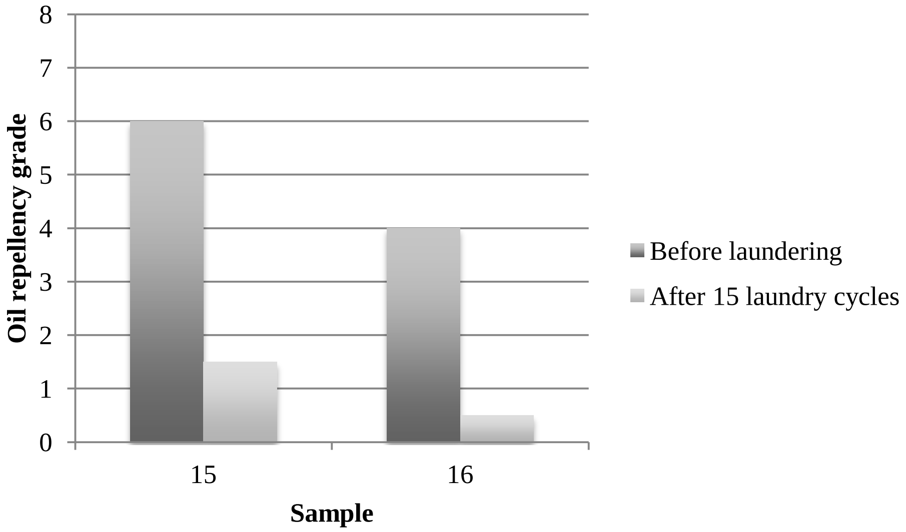

Figure 15: Results from the oil repellency test for samples treated with a FC-concentration of 5 g/l (Sample 15) and samples treated with a combination of dendrimer and FC (Sample 16). The oil repellency was evaluated before laundering and after 15 laundry cycles

When comparing figure 15 with figure 13 it can be seen that the oil repellency of sample 16 was lower before laundering than for the other samples. From figure 15 it can be seen that sample 16 has lower oil repellency than sample 15 both before and after laundering. After 15 washes there is practically no oil repellency left for those samples. An explanation may be that some of the dendrimers covers the fluorocarbons, thereby giving higher surface energy and thus lowering the repellency effect. It is also possible that the reactivity between the surface and the dendrimers are lower than between the surface and the fluorocarbons.

4.5 Contact angle measurements

Contact angle measurements were performed on samples 1, 10, 17 and 18 in order to evaluate if it can be used as a complement when the spray test is not accurate enough to distinguish between samples. It might be possible to detect differences between samples that obtain the same water repellency grade from the spray test. The results from the contact angle measurements of the samples before laundering can be seen in figure 16.

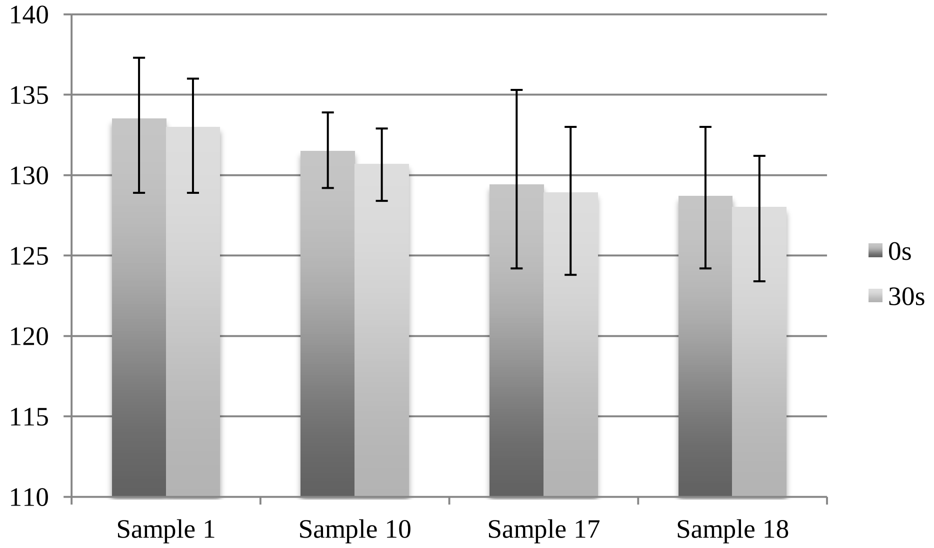

Figure 16: Results from the contact angle measurements for plasma treated samples (1 and 10) and conventionally treated samples (17 and 18). The contact angles after 0 seconds and after 30 seconds are presented, as average values of three measurements (left and right angle in each case), and the standard deviation given as error bars.

It can be seen from figure 16 that the contact angles are higher for sample 1 and 10 than for sample 17 and 18. Sample 1 and 17 obtained the same water repellency grading from the spray test. But it could be seen that there were a tendency of very small droplets on sample 17. This observation corresponds well with the results from the contact angle measurements which shows that sample 17 have a somewhat lower water contact angle than sample 1.

Another observation that could be made during the contact angle measurements was that all the droplets on sample 1 and 10 and some droplets on sample 17 and 18 were slightly shaking on the samples, as they were applied. It could be that those droplets were in the desirable Cassie-Baxter state i.e. non-wetted cavities. When the contact angle decreased to around 125° or lower, the droplets did not move which is an indication that they were in the Wenzel state. This could be seen for some measurements for sample 17 and 18. This could explain why there was a small adherence of droplets on sample 17 in the water spray test, if the droplets were in the Wenzel state they would not roll-off as easily even though the water repellency is high. For sample 1 and 10, on the other hand no drop adherence could be seen in the water spray test, probably thanks to formation of a Cassie-Baxter state. It is also noticeable that sample 17 and 18 show larger spreading in the results, indicating that the finishing is not as even for those samples as for sample 1 and 10. These results also indicates that the plasma treatment have a positive effect on the repellency even before laundering or abrasion and may be used as a faster evaluation method than washing and spraying since differences between the samples can be detected on an earlier stage. Contact angle measurements were also performed on the washed samples. Unfortunately, washing made the fabric surface too rough to detect the measurement baseline in a reliable way and those measurements are not included in this report.

4.6 Stain repellency

The stain repellency was evaluated for sample 15 and 16 in order to determine whether the addition of dendrimers had influence on the repellency of common dirt. The remaining stains on sample 15 and 16 were compared. It could be seen that sample 15 showed more repellency than sample 16 towards chocolate but for orange juice and coffee no distinct differences could be seen. Hence, the dendrimers did not provide any addition to the repellency effect.

4.7 Bonding between polyamide and fluorocarbon

The reactions between the surface and the fluorocarbon polymers are probably the reason for the increased durability of the fluorocarbon impregnation. Amide linkages in the polyamide structure are broken during the plasma treatment, forming carboxylic acids and amine groups [45]. The plasma treatment may also introduce hydroxyl groups to the surface. These groups will function as active sites on the surface and can react with functional groups on the fluorocarbon polymer, forming covalent bonds and dipole interactions. The functional groups on the fluorocarbon polymer are presented in figure 17.

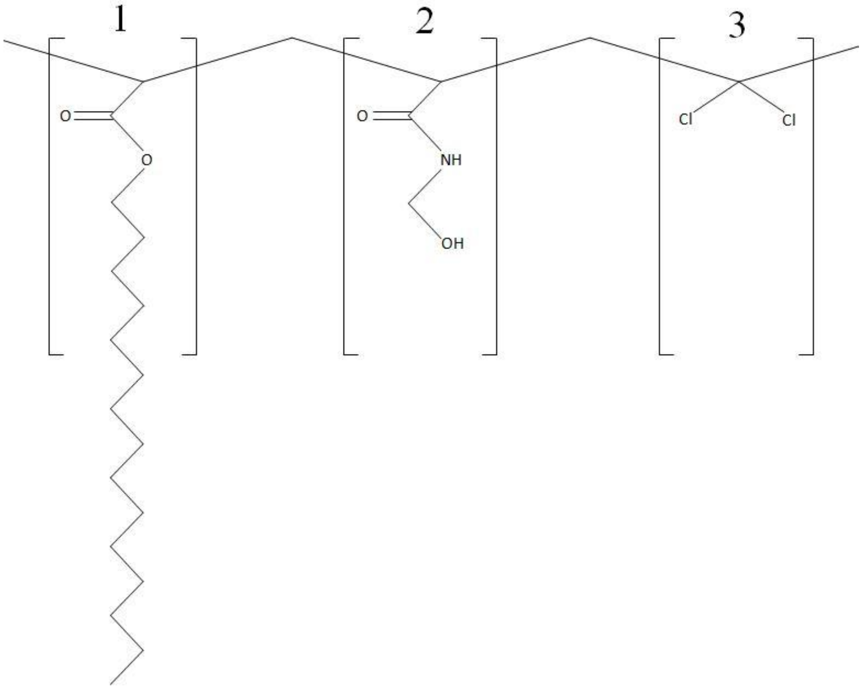

Figure 17: Functional groups of the fluorocarbon polymer that might react with active sites on the polyamide surface.

The dendrimer based chemical only contains hydrocarbon sections and no functional groups that will react with the active sites on the surface [46].

5. CONCLUSIONS AND FUTURE WORKS

Atmospheric plasma treatment is a promising technique for surface treatment of textile fibers. The results from this study shows that the use of atmospheric plasma treatment makes it possible to lower the chemical amounts needed to obtain the required oil and water repellency of polyamide fabrics. The fluorocarbon concentration could be lowered to 1/3 of the concentration used in typical commercial processes, when atmospheric plasma was used as a pre-treatment compared to when conventional finishing was performed. Samples that were pre- activated with atmospheric plasma had a better washing durability than samples that were treated with conventional wet chemical treatment. It could be clearly seen that the plasma pre-treatment had a positive effect on the durability of the impregnation, when comparing conventionally treated samples with plasma treated samples of the same FC-concentration. A conclusion that can be drawn is that the plasma treatment enhances the impregnations endurance towards washing. This is in line with the inherent properties of plasma treatment of polymeric surfaces, in which functional groups are introduced on the surface. In this case such groups work as binding sites between the fabric and the FC- molecules.

Theoretically, it should be possible to use dendrimers to reduce the fluorocarbon concentration since it could be seen that the water repellency is lowered more than the oil repellency when the fluorocarbon concentration is lowered. This indicates that dendrimers could be used to increase the water repellency. However, in this study, the oil repellency decreased when dendrimers were added and no significant increase in water repellency was observed. This is probably because the dendrimers partially covered the fluorocarbons. Further studies could be made where the application of the chemicals is controlled and to make the fluorocarbons the outermost layer should be a feasible way forward. It could also be interesting to use functionalized dendrimers that can bind to the active sites on the fabric.

Since the conventional way of impregnating fabrics consumes a lot of water and chemicals it could be interesting to use another way for the application of chemicals in order to decrease the environmental and health impact even further. One alternative is to use spray for the fluorocarbon finishing after plasma treatment. In that way only the surface would be treated instead of the whole fabric, which will happen when wet chemical treatment is used. It could also be interesting to evaluate a treatment with fluorocarbon plasma.

Since concentrations of fluorocarbons as low as 5g/l showed good but varying results it could be interesting to change its molecular structure, so that the fluorocarbon concentration remains at the same level, as for the 5 g/l dispersion, but the polymeric backbone concentration increases. That could give a more even distribution of the fluorocarbons over the surface, hence giving a better finish.

Future works could also evaluate the resistance of the finishing towards a combination of washing and Martindale abrasion. In this study the Martindale abrasion was too aggressive to give informative results. A conclusion to be drawn is that the abrasion would need to be less destructive in order to see any differences in the behavior between the samples. Alternatively, a lower number of washing cycles could be combined with the Martindale abrasion. In this study the samples were washed 20 times before Martindale abrasion and consequently the aging of the finishing was already high.

Contact angle measurements can be used to evaluate the hydrophobic behavior of the textiles when the differences cannot be detected with the spray test or oil repellency test. Future studies could also include roll-off angle measurements since that is a good way of measuring superhydrophobicity.

The reactions that take place between the plasma constituents and the polyamide surface are also of interest and future research could include evaluating the surface reactions by using methods like ESCA and FTIR.

This study has shown that atmospheric plasma treatment is a potential method for reducing the use of perfluorinated compounds in outdoor garments. If this kind of treatment could be used in industry, lower amounts of chemicals would be needed for the impregnation of garments and consequently lower amounts would be released to the environment.

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