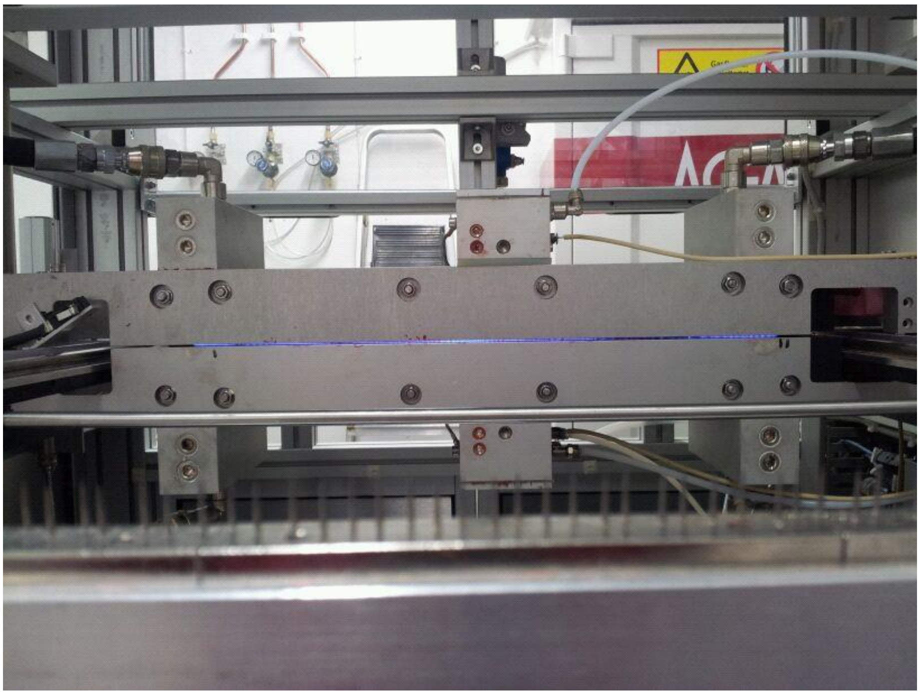
CHALMERS



# Water- and Stain-repellent Textiles, Using New Plasma Technology

*Master of Science Thesis in the Master Degree Programme Materials and Nanotechnology*

DANY SOUMA

Department of Chemical and Biological Engineering
*Division of Applied Surface Chemistry*
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden, 2012

Master of Science Thesis

# Water- and Stain-repellent Textiles, Using New Plasma Technology

DANY SOUMA

Examiner: Prof. Krister Holmberg
Supervisor: Dr Philip Karlsson

This work has been performed at Swerea IVF and Chalmers University of Technology

Department of Chemical and Biological Engineering
Division of Applied Surface Chemistry
Chalmers University of Technology
Göteborg, Sweden 2012

Water- and Stain-repellent Textiles, Using New Plasma Technology
DANY SOUMA

Department of Chemical and Biological Engineering
Division of Applied Surface Chemistry
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Telephone: +46 (0)31–7721000
Göteborg, Sweden 2012

Water- and Stain-repellent Textiles, Using New Plasma Technology
DANY SOUMA
Department of Chemical and Biological Engineering
Chalmers University of Technology

## ABSTRACT

New technology is sought after in the process of hydrophobizing textiles since the conventional method of obtaining these features includes a pad-dry-cure sequence which consumes a lot of energy as well as chemicals. Hydrophobization is used as a common name for water-, oil and stain repellency and is a desirable feature in many textile applications.

In this thesis a new technique of hydrophobizing textiles is evaluated, using Atmospheric Pressure Plasma (APP) which has the potential to be more cost-effective and environmentally friendly compared to conventional treatments. Some vacuum plasma trials were also conducted.

Fluorocarbon-based chemicals were used since their use is a prerequisite to achieve oil-repellency on fabrics. To achieve the best results the fluorocarbons were used in their concentrated form, but diluted baths were also evaluated. The fabrics were immersed in an aqueous dispersion of fluorocarbons, squeezed between rollers and dried over night at room temperature before being plasma-treated. Some samples of wet fabric were plasma-treated as well.

The plasma-treated samples were first evaluated by measuring the water contact angle of the fabrics. The oil repellency was tested before and after the fabrics had been exposed to simulated wear, using a Martindale apparatus. The samples were also sprayed with water in a standardized way, to test the water repellency. Environmental Spectroscopy for Chemical Analysis (ESCA) and Scanning Electron Microscopy were used to evaluate the effect of the plasma treatment.

The results showed that it is possible to hydrophobize textiles with the use of an APP, but that rather high concentrations of the fluorocarbons are needed. The results also showed that the oil repellency was greater for the plasma treated samples compared to the conventional ones after simulated wear, which might be due to the fact that the fluorinated compounds bind harder to the substrate when exposed to the plasma. The latter was shown by the ESCA results, which indicated covalently anchored fluorocarbons to the fabric surface.

# Acknowledgements

Firstly, I would like to thank all employees at Swerea IVF in Mölndal for their support and guidance. I hope I did not cause you too much trouble.

Special thanks go out to my supervisor Dr Philip Karlsson which have shown not only great interest in my work but also aided me with different views on problems that occurred during the diploma work. I am very thankful for all that he has done for me, and could not be any happier with the support I received.

I would also like to thank FOV Fabrics AB in Borås for providing me with both the fabric and some of the chemicals used in the thesis, Ms Anne Wendel at Chalmers University of Technology for her help with the ESCA measurements, Mr Jan Johansson at Swerea IVF for taking the SEM pictures and Prof. Krister Holmberg for his advice and allowing me to use the apparatus at the University. Finally I would like to thank my family and friends for all the support and love, I am truly blessed.

# Table of Contents

# 1 Introduction

## 1.1 Background

The demand for high functional textiles is a steadily increasing market for the textile industries [1]. Since most of the textile manufacturing is made in Asia, where labor costs in general are much lower, the Swedish industries need to either optimize their production or differentiate their products in order to compete on the market. New technology is therefore requested to gain increased market shares and the use of plasma technology might be the answer to get products with outstanding properties, manufactured in more cost-effective processes.

Plasmas technology was introduced to the industry during the 1960s and was initially used by the micro-electronics industries. The number of applications was increased in the 1980s to also include surface treatments of polymers and metals [2]. Several properties of a material surface can be affected by the use of plasma, for instance enhanced wettability, hydrophobicity, sterilization and activation of an inert surface to enable surface reactions with functional groups. Those possibilities along with a positive economical aspect of plasma technology, as utilized by the micro-electronics industries have been a key factor to attempt to implement the plasma technologies elsewhere, such as in the textile industry.

Two important properties that are of high value for many types of textiles are their ability to repel water and soil. The conventional method of producing these features includes very energy-consuming processes i.e. washing and drying of the fabric. There is also a high consumption of chemicals involved, since the fabric needs to be impregnated by a solution of hydrophobizing agent. Several compounds can be applied to a textile in order to obtain hydrophobicity, e.g. waxes, silicones and silanes, they are however unsuccessful for soil- repellency. Fluorocarbons on the other hand are excellent in repelling water and oil, due to their low surface energy [3].

The disadvantages with fluorocarbons, besides being more expensive than other hydrophobizing agents [3], are the health and the environmental concerns involved with their use. Studies have shown that perfluorinated chemicals can be accumulated in living organisms, affecting fertility and hormone functions and that they accumulate in ecosystems [4]. Consequently, a minimization of the quantities of these chemicals in the production line would not only be ideal from an economical point of view but would also be an environmental benefit. Plasma technology could hold the answer to these problems.

## 1.2 Aim

The aim is to develop a new finishing process for hydrophobization of textiles, by the use of atmospheric pressure plasma (APP), with equal or better results compared to current wet treatments. Tests will be conducted on an untreated woven PET-fabric, and a reference sample of the same fabric, but that had been finished with fluorocarbon chemicals in a conventional way.

Initial trials will be conducted on a vacuum plasma unit with different process gases and a fluorocarbon chemical typically used in conventional finishing processes. The main focus however will be on the APP with helium being the main process gas tested; due to safety considerations fluorocarbons in gas phase will not be evaluated. The fabric will be pretreated by different fluorinated chemicals in an attempt to graft and crosslink fluorocarbon moieties on the surface of the fabric. Helium works as an activating agent, introducing polar groups to the surface, and does not contribute to the level of hydrophobisation.

The plasma technology has great potential to limit the environmental impact of textile processing; this is possible primarily due to less use of energy and water compared to the wet treatment techniques. Also, the amount of possibly hazardous chemicals that are used when impregnating the textiles could be reduced. Therefore plasma technology is likely to contribute towards a more sustainable development of the textile industry.

# 2 Theory

## 2.1 Textiles

Textiles can be made of fibers, which can be of natural or synthetic origin. Examples of natural fibers are cotton, silk or wool while common synthetic fibers are polyesters, acrylics and nylons. The synthetic fibers are an important part of the textile industry with a yearly production that surpasses the amount of cotton produced [5]. Polyester is produced in the largest quantity of all synthetic fibers worldwide with a volume of 21 million tons in 2002 and the primary market being textiles for apparel [6].

### 2.1.1 PET fibers

Approximately 95 % of all polyester fibers manufactured today is polyethylene terephthalate (PET), the reason for this being its low cost, convenient processability and its excellent and tailorable performance [6][7].

The chemical structure of the PET fibre is characterized by the presence of carboxylate ester groups and benzene rings which makes the molecule rigid and fully extended due to the short hydrocarbon chains separating them [8]. See figure 1 for chemical structure.

Polyester fiber was commercially produced for the first time in England in 1941, by condensation of ethylene glycol (1,2-ethanediol) and terephtalic acid(1,4-benzenedicarboxylic acid)[8] forming PET.

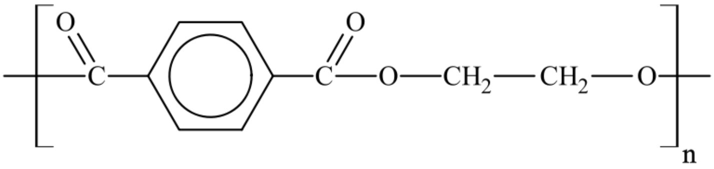


Figure 1 Chemical structure of PET.

Today PET is made in a transesterification reaction between ethylene glycol and dimethyl theraptalate. The dimethyl theraptalate is allowed to react with an excess of ethylene glycol with sodium methoxide working as a catalyst. This forms bis(2-hydroxyethyl) theraptalate and methanol. The methanol is removed by distillation, and the bis(2-hydroxyethyl) theraptalate is heated to induce further transesterification which then forms the polymer and releases ethylene glycol. The molten polymer is extruded to a thick band, cooled and chipped. The chips are re-melted under nitrogen atmosphere and spun into fine filaments, which make up the polyester yarn [8].

## 2.2 Hydrophobization

In order to fully understand the phenomena of hydrophobization and stain repellency of textiles one must know the basic concepts of surface energy. To achieve a hydrophobic surface, the interactions between water and the surface should be inhibited. Such inhibition is achieved by minimizing the polar components of the surface energy , i.e.van der Waals forces, electrostatic interactions and hydrogen bonds.

### 2.2.1 Surface energy

The surface energy is a concept that can be used to describe the ability of a liquid to wet a surface. All materials have a specific surface energy, which magnitude depends on the molecules making up the same (the molecules ability of the solid and liquid to interact with each other). A high interaction between these molecules results in a high surface energy and vice-versa for a low interaction. Hydrogen-bonds and induced dipoles create strong interactions between the surface and the liquid. Wetting is easier accomplished on surfaces with high surface energy since the solid is then more prone to interact with the liquid. To illustrate this we can use Teflon, $(\text{-CF}_2\text{-CF}_2\text{-})_n$ ,as an example; Teflon consist of fluorinated hydrocarbons which are unable to create hydrogen bonds nor induced dipoles and has a surface energy of 20 mN/m and to be able to wet this surface a liquid with a surface tension below this value is needed. Water, which has a surface tension of 72 mN/m, will not successfully wet such a surface.

Other factors that are of significance when wetting surfaces are the surface structure, i.e. porosity, roughness and chemical heterogeneity.

*Young's equation*

The different surface forces involved in spreading of a liquid on a surface can be seen in Figure 2. This phenomenon of spreading is described by Young's equation, Eq. 1, where $\gamma_{SG}$ is the surface free energy of the solid, $\gamma_{SL}$ interfacial tension between the solid and the liquid and $\gamma_{LG}$ is the surface tension of the liquid. The contact angle of the liquid on the surface also needs to be determined.

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta_c \qquad (Eq. 1)$$

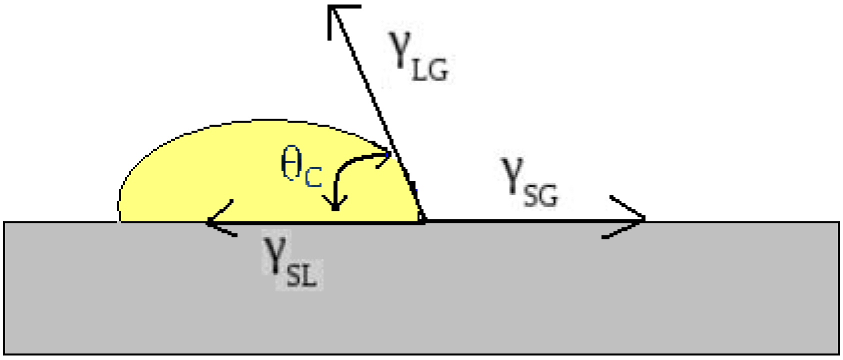


Figure 2 Surface forces involved when a liquid interacts with a substrate.

Another way of depicting the Young equation is by the use of a spreading coefficient, S (Eq.2), where spreading occurs if S > 0.

For a surface to be considered hydrophobic the contact angle of the liquid should exceed 90 °. The contact angle of a drop can be measured directly by placing a drop horizontally on a substrate, also known as the sessile drop method, or by an adhering gas bubble captured at a solid-liquid interface [9].

$$S = \gamma_{SG} - \gamma_{SL} - \gamma_{LG} \qquad (Eq. 2)$$

The concept of critical surface tension ($\gamma_c$) can be used to determine the surface energy of a solid. The most straight forward way to do this is by a Zisman plot, which is done by measuring the contact angles of a series of liquids with decreasing surface tensions. Cosine of the contact angle is then plotted against the surface tension of the liquid and the critical surface tension is defined as the point where the plotted line intersects with the zero contact angle [9].

### 2.2.2 Hydrophobizing agents

Hydrophobic properties of a surface can be achieved by the use of hydrophobizing agents such as paraffin waxes, silicones, silanes and fluorinated polymers [9]. Since textiles normally have a negative net charge, cationic surfactants with e.g. methyl or fluorine groups can also be used. Surfactants also have a debonding effect which reduces the fibre-fibre interaction [9]. The majority of these hydrophobizing agents are ineffective in soil repellency since their surface energy is not low enough. This problem is solved by using fluorocarbon-based chemicals e.g. Teflon, which have the lowest surface tension among common polymers [3]. In Table 1 the surface energy of different functional groups can be seen

**Table 1. Critical surface tension ($\gamma_c$) for different surface groups at 20 °C [9].**

| Surface groups | $\gamma_c$ (mN/m) |
|---|---|
| **Hydrocarbon surfaces** | |
| -$CH_2$-$CH_2$- | 31 |
| -$CH_3$ (monolayer) | 22-24 |
| -$CH_3$ (crystal) | 20-22 |
| **Fluorocarbon surfaces** | |
| -CFH-$CH_2$- | 28 |
| -$CF_2$-$CF_2$ | 18 |
| -$CF_2H$ | 15 |
| -$CF_3$ | 6 |

*Fluorocarbons*

Fluorocarbons have been used in the textile industry since the 1950s, thanks to their outstanding properties as repellants for water, oil and grease [3][10]. As stated previously, fluoropolymers owe their special properties to their low surface energy which means that they not only repel water but also oil-based substances. Fluoropolymers suited for textile finishing generally consists of a polymeric backbone, e.g. acrylate or polyurethane, with fluorinated side chains. Their effectiveness for each application varies with chain length, the shape of the chain and the type of end groups of the fluorinated side chains [10].

A perflourinated compound that is frequently occurring for hydrophobisation of textiles is perfluorooctanoic acid (PFOA), which is a chemically stable surfactant. PFOA will generally be denoted C8 in this thesis. A desire, however, has grown to phase out this chemical since studies has proven it to be very persistent in the environment, it causes adverse effects on laboratory animals and low levels of it has been found in the environment and in the blood of the general U.S. population [11]. Therefore a majority of the Swedish textile manufacturers have switched from the

C8 based fluorocarbon to a C6 based one. The latter are classed as non-bioaccumulative, since they are more easily broken down in the environment.

### 2.2.3 Legislation

The Swedish legislation regarding chemicals is governed by REACH (Registration, Evaluation, Authorization and Restriction of Chemicals), CLP (Classification, Labeling and Packaging) and by the Swedish Environmental Code (Miljöbalken). REACH and CLP are European Union regulations and they classify knowledge and labeling requirements for all chemical substances manufactured in or imported into the EU. REACH also evaluates potentially hazardous chemicals and establishes licensing requirements or limitation of use for chemicals [12]. The Swedish Environmental Code is much broader and consists of seven chapters with general and specific rules to assure the safety of the general public.

The majority of the fluorocarbon-based chemicals are not regulated in any way, there are some specific ones that are forbidden to sell, use or manufacture. Perfluorooctanesulfonic acid (PFOS) is one of those which use is restricted by the EU in regulation number 850/2004. The phasing out of PFOS occurred voluntarily from the manufacturers due to this concern. In 2006 eight major chemical manufacturers also agreed to phase out the production of PFOA by 95 % by 2010 and a complete stop of production by 2015 [11].PFOA is known to have high persistency, bio-accumulativity and toxic effects, but is not regulated in any way [13].

In the 90’s Oeko-Tex was developed as a response to consumer-desires for environmentally friendly clothing. Oeko-Tex is a standard for environmental certification of textile products. Bluesign is a standard with similar scope, which was developed a few years back. A textile manufacturer who wants these kinds of certifications needs to reach the demands for the use of certain chemicals. In both Oeko-Tex and Bluesign the use of PFOS/PFOA have low threshold limits, only trace amounts are allowed [14][15].

## 2.3 Conventional method for hydrophobisation of textiles

The conventional method of hydrophobizing a textile involves a wet treatment step. The method usually consists of a pad-dry-cure sequence (see Figure 3). This method is used because of its excellent ability to impregnate fabrics homogenously [7]. In the padding step the fabric passes through a bath of an aqueous dispersion of hydrophobizing chemicals. The concentration of these chemicals is usually between 2-10 %. The bath is followed by squeezing of the saturated fabric between two rollers with a specific pressure, to ensure that the fabric obtains a certain pickup. Hence, the pickup is a measure of the amount of hydrophobizing chemicals that is absorbed by the fabric and is normally expressed by the following equation:

$$Pickup\ \% = \frac{Rolled\ weight\ of\ the\ fabric - Dry\ weight\ of\ the\ fabric}{Dry\ weight\ of\ the\ fabric} \qquad Eq.3$$

For diluted baths a modified version of Eq.3 can be used:

$$\frac{\text{Mass Chemical [g]}}{\text{Mass Fabric [g]}} = \frac{(Rolled\ weight\ fabric - Dry\ weight\ fabric) \times Weight\ Chemical}{Total\ weight\ of\ chemical\ bath\ (Diluent + Chemical) \times Dry\ weight\ fabric} \quad \text{Eq. 4}$$

The padding and squeezing is followed by a drying step, to remove the excess water before curing it at a higher temperature. A high temperature is needed to fix the chemicals on the fabric surface.

The pad-dry-cure technique makes the chemicals spread evenly in the fabric, but there are some downsides. The treatment consumes large quantities of water and chemicals. It also involves high energy costs due to the drying and curing of the fabric at high temperature. Plasma technology has great potential to substitute finishing processes like this, thus reducing the costs and the environmental impact [16]. Plasma technology is further described in the next section.

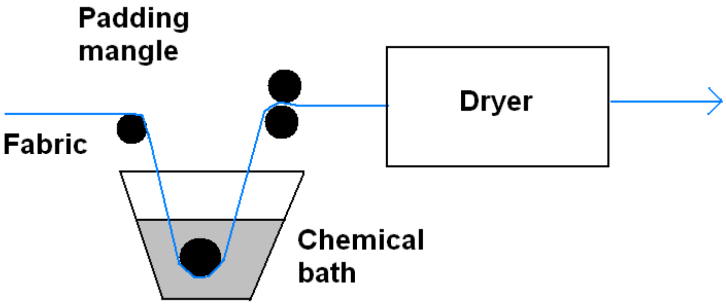


Figure 3 The Pad-dry-cure sequence is a conventional method of hydrophobizing textiles.

## 2.4 Plasma

Plasma, also known as the fourth state of matter, is defined as ionized gas and consists of electrons, neutrons, ions, radicals, electronic excited particles and UV-radiation. It is created by introducing energy to a gas which causes a reorganization of the electronic structure of the atoms and molecules [17]. The energy source can either be thermal, consist of an electric current or electromagnetic radiation.

Plasmas can be divided into two broad categories:

- Thermal plasmas have high-energy densities and all of its constituents have the same relative temperatures. The sun is an example of a thermal plasma.
- Non-thermal plasmas have lower energy density and is characterized by a difference in temperature between electrons (which have energies that corresponds to several 1000 °C) and heavier elementary particles, which have a temperature just above room temperature.

Common thermal plasmas are torches which consist of two electrodes generating a plasma arc sustained by means of an electric dc current flowing through the body of the discharge Thermal plasmas are often used in materials processing, since they have a high energy density, they are used to heat, melt or even vaporize materials [18].

Non-thermal plasma or “cold plasma” is also used in materials processing but for plasma etching, deposition processes and in plasma surface modifications [18], since its low temperature makes it nondestructive to most materials, including polymers and textiles. The group of cold plasma can be further divided into vacuum plasma and atmospheric pressure plasma (the latter can also be used as thermal plasma).

### 2.4.1 Vacuum plasma

A vacuum plasma is generated by keeping gas under sufficiently low pressure and applying electromagnetic energy, thus ionizing some of the atoms and radicals. The pressure at which the samples are processed varies with the type of energy source used. For the radiofrequency range the working gas pressure is kept fairly low, approximately in the 0.1 mbar range, whereas for a microwave source the working gas pressure is higher, between 0.5-1 mbar [19].To maintain such low pressures a vacuum system is needed which constitutes the major expense in plasma devices [20]. Another issue is the fact that only batch-wise production is possible; also the sample needs to be compatible with vacuum. Since most textiles are produced in a continuous process, the vacuum plasma might not be as well suited for this type of industry as an atmospheric-pressure plasma.

### 2.4.2 Atmospheric pressure plasma (APP)

APP can be both thermal and non-thermal depending on the density of the feeding power. To obtain non-thermal plasma a pulsed power supply or a low density of the feeding power is needed [17]. There are three types of APP technologies that are relevant for textile treatments – the Corona discharge, the Dielectric Barrier Discharge (DBD) and the Atmospheric Pressure Glow Discharge (APGD). Their modes of generation are depicted in Figure 4.

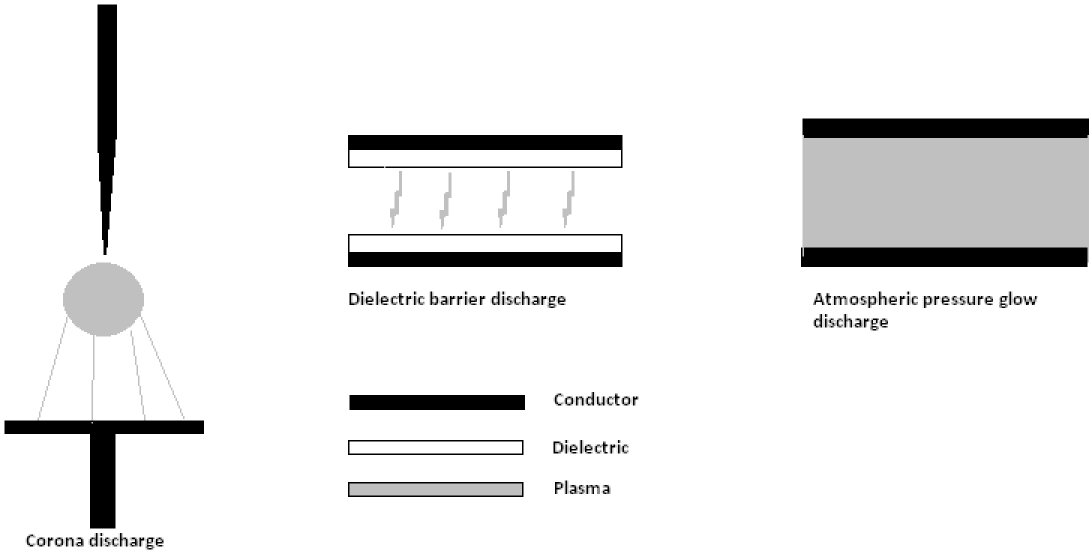


Figure 4 The plasma generation of corona discharge, DBD and APGD. Picture redrawn from [21]

### Corona treatment

Corona discharge is the most commonly used plasma process and it is generated from a high-voltage electrode which forms bright filaments that extends towards the substrate. Coronas are however very weakly ionized and non-uniform in their sample treatment. When it comes to textiles, the plasma energy can merely affect loose fibers and does not penetrate deeply into yarn or woven structures [2].

### APGD

The characteristics of this type of plasma are similar to the low-pressure glow discharge plasma which is the most popular plasma in the microelectronics industry. The plasma is generated over two symmetrical electrodes by applying a relatively low voltage of approximately 200 V. It has a higher power density compared to both the DBD and the corona treatment and forms a uniform, homogenous glow in the area between the electrodes. To avoid the generation of a hot plasma arc, which would harm sensitive materials like textiles, there is a need to use an inert process gas such as He or Ar, as a preventive measure [2] [21].

### Dielectric Barrier Discharge

The DBD system is comprised of two symmetrical electrodes which are covered by a dielectric material (e.g. ceramic or glass) and the plasma is generated by applying a high voltage (1-20kV). The dielectric is needed to prevent the plasma to discharge as an arc. This forces the plasma sheath to spread over the electrodes instead of burning straight through the fabric, giving rise to damages. The DBD forms uniform plasma and has a higher electron density than the corona treatment (but not as dense as the glow discharge) and is therefore the most promising plasma technology for textile processing [21].

### 2.4.3Modification of textile surfaces with plasma

When the plasma is formed it contains charged species, neutrons, electronic excited particles and electromagnetic radiation which is emitted as UV- and IR- light. The species formed in a plasma can have several effects to the outermost chemical groups of a given substrate:

- Crosslinking
- Etching
- Deposition/Grafting
- Functionalization

The parameters of the plasma such as the choice of process gas, will determine which of those four mechanisms that will be the dominating one. For example, to create a hydrophobic surface fluorocarbon based gasses may be used, while the use of oxygen will activate the sample surface thus making it more hydrophilic [22]. The radicals formed in the plasma react with the chemical groups on the surface of a material. This chemical reaction is used to functionalize a material surface, creating new properties of the material without changing the bulk properties, such as softness and strength etc.

When using small fluorocarbon molecules for plasma treatment it has been shown that etching and grafting/polymerization will be two conflicting mechanisms, where the fluorine carbon ratio of the monomer gas will determine the dominating mechanism. For $CF_4$ gas the etching mechanism will be dominating while polymerization will be favored for lower F/C ratios [23].

Commonly used process gases are argon and helium which both tend to give the treated surface a hydrophilic character. The reason for this is the incorporation of oxygen from the surrounding air that tends to be reactive, although present in low concentrations. For the nitrogen, present in higher concentrations however, studies have shown that its incorporation at the surface is barely detectable, when using argon or helium plasma. Thus leading to the conclusion that an increase of the hydrophilicity on the substrate cannot be related to nitrogen in the same way as for oxygen [24]. Argon does not have those properties and for this reason gives less stable plasmas.

There are however some difference in the properties of He and Ar. Helium is a very simple atom with only two electrons and two protons and it has the highest ionization potential but also a large ionization cross section, meaning that the possibility of a helium atom to be ionized is high upon collision with other components of the plasma. The large ionization cross section of helium is a consequence of its simple structure, leaving no room for other types of excitations than ionization. Helium also has an excellent heat conduction which makes it discharge homogenously. This makes helium well suited for producing a cool and homogenously distributed atmospheric plasma with a large volume and free from discharges that would possibly damage the textile [21].

There are several methods that can be utilized along with the plasma processing to functionalize a textile surface, for example to make it more hydrophobic. The most straightforward method is to use a non-depositing gas which exchanges single atoms of the polymer fiber atoms with more hydrophobic ones, such as fluorine groups. Another method is to immerse the textile in a solution of hydrophobic pre-polymer initiator and then expose the fabric to the plasma. This leads to a grafting of the pre-polymer on the textile surface.

Another option is the deposition of a polymer at the fiber surface, directly in the plasma zone. This method can be done in two different ways; either as a simultaneous deposition of the polymer and plasma treatment (plasma polymerization) or in a two step process. In the two step process the fabric is first exposed to the plasma (Ar or He-based) which creates radicals at its surface. Then unsaturated polymers are introduced which reacts with the radicals on the substrate surface (plasma grafting) [25]. The method works in the opposite way as well that is, the polymers may be introduced prior to plasma treatment.

### 2.4.4 Comparison between wet treatment and plasma treatment

A comparison between plasma treatment and the conventional method used to hydrophobize a textile (Table 2) clearly show the benefits of the plasma treatment, where the major advantages being the low water and energy consumption. Other advantages of the plasma includes its versatility (any type of fabric can be treated), low consumption of chemicals and the optimization of the surface properties without affecting the bulk characteristics [23].

There are some disadvantages though; it is in most cases impossible to calculate the physical and chemical behavior of a plasma due to the huge amount of elementary reactions that occur. For this reason, the exact chemical composition of the surface is hard to predict, and it is also difficult to limit the type of functional groups formed, to a well defined set of species. [23].

**Table 2. Comparison of plasma treatment to a typical conventional method [15].**

| **Parameter** | **Plasma** | **Conventional method** |
|---|---|---|
| **Solvent** | None (gas phase) | Water |
| **Energy** | Electricity | Heat |
| **Type of reaction** | Complex | Simple |
| **Deepness of the treatment** | Very thin layer | Bulk of the fibers |
| **Water and energy consumption** | Low | High |

## 2.5 Characterisation methods

This section provides a short introduction to the main characterization methods used to determine the hydrophobicity of a textile.

### 2.5.1 Contact angle measurement

A high water contact angle is a typical sign of a hydrophobic surface. A commonly used method to measure the contact angle of a drop resting on a horizontal plane is the sessile drop method. The method utilizes a goniometer to measure the contact angle and a microscope objective to view the angle directly. The droplet is placed on the surface of the substrate and a camera captures a picture of the drop. The profile of the droplet is analyzed by an image analysis software, which calculates the static contact angle. However, it can be quite difficult to get a representative value of the contact angle for surfaces that are rough or heterogeneous. This is solved by measuring the dynamic contact angle, which is done by measuring the advancing and receding contact angle. When measuring the advancing and receding contact angle to obtain the dynamic contact angle the deposited droplet volume is increased with constant speed and then decreased. The angle calculated during the increase is the advancing contact angle and the angle that is calculated at the decrease is the receding contact angle. These values can be used to calculate the contact angle hysteresis which indicates the high- and low-energy parts of a heterogeneous surface [16][9].

### 2.5.2 Spray test

Spray test is a method to determine the resistance of fabric to wetting by water. It is commonly used to measure the water-repellent effect of finishes applied to fabrics. The test is conducted by spraying water against the surface of the fabric specimen under controlled conditions. This exposure will lead to wetted patterns on the fabrics which are graded against a standard chart.

### 2.5.3 Oil repellency test

The oil repellency test is used to determine how well a fabric specimen will repel oils of different surface tension. The test is conducted by placing drops, from a series of liquid hydrocarbons, onto the substrate and then observing the wetting, wicking and contact angle. The test liquids are numbered so that increasing numbers mean decreasing surface tension and the test is started with the test liquid of lowest number hence, highest surface tension. The oil repellency is described as the highest numbered test liquid which does not wet the fabric.

### 2.5.4 Martindale abrasion test

The Martindale test is used to determine the resistance to abrasion of the fabric. This is done by mounting fabric specimen in a special apparatus and rubbing them with a certain pressure, for a number of cycles, against a standardized wool fabric.

### 2.5.5 Scanning Electron Microscopy (SEM)

A SEM can be used to greatly magnify objects by means of electrons. An electron beam bombards the surface of the specimen and the emitted electrons from the bombardment are detected. Those are backscattered primary electrons, secondary electrons, Auger electrons and electrons of the continuum. The backscattered and secondary electrons are the ones that are used to create the image of the substrate [26].

A tungsten filament with a low beam current is a common detector for the backscattered primary electrons and to be able to detect the backscattered and secondary electrons silicon diodes and a Thornley-Everhart scintillator respectively could be used [26].

### 2.5.6 Environmental Spectroscopy for Chemical analysis (ESCA)

ESCA is a surface-sensitive technique utilized to provide quantitative information of the chemical structure, atomic composition and chemical bonding state. Since the measurement is conducted in vacuum, only specimens that will not be affected by low pressure can be evaluated.

An ESCA measurement is done by bombarding the surface with X-ray photons with known energy, *hv,* and by determining the intensity distribution as a function of kinetic energy for the photoelectrons that has been expelled from the sample surface. The binding energies can then be calculated by the energy conservation law of the photo electric effect $E_K = hv - E_B$, where $E_B$is the binding energy of the photoelectrons and $E_K$is the kinetic energy of the corresponding photoelectrons. The binding energy is characteristic of the atomic number of the emitting atom and can be used to determine the functional groups on the surface [26].

# 3 Materials and Methods

## 3.1 Materials

The conventional finishing as well as the plasma treatments was conducted on a polyester filament fabric (Table 3) provided by FOV fabrics in Borås. FOV also provided a conventionally hydrophobized PET fabric of the same type, to work as a reference. A reference sample was also made the conventional way at Swerea IVF. The sample was immersed in dispersion number 3 (Table 7), calendered, dried in R.T. overnight and then cured in oven at 160°C for 1 min.

**Table 3. Properties of the polyester filament fabric**

| **Polyester filament fabric** | |
|---|---|
| **Construction** | 100% PET filament fiber |
| **Weight** | 126.5 g/m$^2$ |
| **No. of filaments** | Warp: 40 Weft: 23 |
| **Filament count in dtex** | Warp:167 Weft:167x2 |

## 3.2 Chemicals

The hydrophobization was done using a fluorocarbon-based chemical in aqueous solution. Three different commercial varieties of fluorocarbons were used as well as one crosslinking agent (booster). RUCO-GUARD AFR6 (AFR6) and RUCCO-GUARD EPF 2023 (EPF 2023) (Table 4) were kindly provided by Rudolf GmbH, Germany, and the two Flexipel products by Vendico Chemical AB, Sweden.

**Table 4. The different chemicals used on the fabrics.**

| **Fluorocarbon compounds** | **Description** |
|---|---|
| RUCO-GUARD AFR6 | Aqueous dispersion of polymer with perfluorinated side chains |
| Flexipel AM-95 | Partially fluorinated polymer, dispersed in water |
| Flexipel S-11 WS | Partially fluorinated acrylic polymer, dispersed in mineral spirits |
| **Cross linking agent (Booster)** | **Description** |
| RUCCO-GUARD EPF 2023 | Blocked prepolymer based on isocyanates |

## 3.3 Plasma treatment

### 3.3.1Vacuum plasma

*Equipment and treatment procedure*

The vacuum plasma treatments were conducted in a Technics Plasma 440 G from Technics Plasma GmbH, Germany. The main component being the reactor vessel in which the sample is placed. Beside the reactor there are four other modules of function: The vacuum system, gas flow system, power supply and pressure measurement system

Physical parameters of the equipment:

- Frequency: Microwave generator, 2.45 GHz
- Max power: 600 W
- Working pressure: ~0.5 mbar
- Gas inlet: 2 gas inlets

The first try to hydrophobize a textile surface was conducted on a 100 % PET textile that was uncolored. The polyester was tested in several ways:

- Purged samples. The purge was conducted by allowing the pressure to drop to 0.24 mbar followed by opening the gas inlet fully for 20 s and eventually shutting of the gas flow, thus allowing the pressure to drop back to 0.24 mbar.
- Without any pretreatment of the fabric or purges of the vacuum chamber.
- Wet samples with no purge of the vacuum chamber.
- Dried and purged samples. Dried in oven at 100 ˚ C for 1 min, to reduce the water content of the fabric
- Pretreated with RUCO-GUARD® AFR6.
- Pretreated with a combination of RUCO-GUARD® AFR6 and RUCCO-GUARD EPF 2023.

Eight samples were plasma-treated according to the parameters in Table 5, and with tetrafluoro methane or argon as the process gas. Some samples were plasma-treated in cycles, thus turning of the plasma in 5 s or 10 s intervals and then turning it back on.

**Table 5. Vacuum plasma parameters**

| Plasma exposure in each cycle [s] | Delay time in each cycle [s] | Number of cycles | Total time of plasma exposure [s] | Power [W] |
|---|---|---|---|---|
| 10 | - | - | 10 | 300 |
| 10 | 5 | 5 | 50 | 300 |
| 30 | - | - | 30 | 300 |
| 30 | 10 | 5 | 150 | 300 |
| 10 | - | - | 10 | 600 |
| 10 | 5 | 5 | 50 | 600 |
| 30 | - | - | 30 | 600 |
| 30 | 10 | 5 | 150 | 600 |

*Untreated polyester*

Samples were cut from a larger specimen and placed inside the vacuum chamber of the plasma equipment. The gas pressure was set to 2 bar and the vacuum pressure was allowed to reach 0.24 mbar before the gas inlet was turned on. The gas flow was set so that the working pressure was 0.7 mbar. When the pressure had stabilized at 0.7 mbar the plasma was turned on. However, the pressure in the chamber was not constant and could increase somewhat during the runs (maximum 0.9 mbar). After the treatment all samples were wrapped and stored in aluminum foil.

*Wet samples*

Samples were cut from a larger specimen and placed in a bath of distilled water where they were kept for two days. They were then padded gently with paper tissue before being placed inside the vacuum chamber and run in the same way as above.

*Purged samples*

Samples were cut from a larger specimen and placed in the vacuum chamber and three purges were conducted prior to the plasma treatment. The purge was conducted by allowing the pressure to drop to 0.24 mbar followed by opening the gas inlet fully for 20 s and eventually shutting of the gas flow, thus allowing the pressure to drop back to 0.24 mbar.

*Dried and purged samples*

Samples were cut from a larger specimen and placed in an oven for 1 min at 100 ˚C before being placed in the vacuum chamber of the plasma. These samples were purged once, according to the procedure described above.

*Hydrophobized samples*

The fabric was first dried for 1 min at 100 ˚C and was then sprayed with AFR6 and a mixture of AFR6 and EPF 2023 (80 wt% AFR6 and 20 wt% EPF 2023). The samples were allowed to dry in a fume hood over night before any further treatment. The dry samples were placed inside the vacuum chamber and were purged according to the procedure described earlier. The pressure was stabilized at 0.7 bar prior to plasma treatment. Plasma treatments were made using either tetrafluoro methane or argon as the carrier gas. Reference samples were also made to evaluate the difference between a conventionally cured and a plasma treated textile. Those samples were cured by putting the sprayed samples in an oven at 170 $^{0}$C for 1 or 5 minutes. Some of the cured samples were plasma-treated with either tetra Fluor methane or Argon as process gas.

Plasma treatment was also conducted on cured samples (1min and 5 min) with either tetrafluoro methane or argon as process gas.

*Further trials with vaccum plasma*

Some further trials were conducted with the vacuum plasma on a colored version of the same PET-fabric. These trials were conducted after promising results had been received with the APP where the samples were immersed in theAFR6 dispersion, instead of applying it as a spray. The plasma parameters used can be seen below (Table 6) and the plasma treatment was conducted in the same way as above with an initial purge, turning on the gas, allowing the pressure to stabilize at 0.70 mbar and then turning on the plasma. The process gas used for these trials was tetrafluoro methane.

**Table 6. Vacuum plasma parameters for the trials that were conducted at a later stage of the project.**

| Sample | Plasma exposure in each cycle [s] | Delay time in each cycle [s] | Number of cycles | Total time of plasma exposure [s] | Power [W] |
|---|---|---|---|---|---|
| 1 | 10 | - | - | 10 | 400 |
| 2 | 10 | 5 | 5 | 50 | 400 |
| 3 | 30 | - | - | 30 | 400 |
| 4 | 30 | 10 | 5 | 150 | 400 |
| 5 | 10 | - | - | 10 | 600 |
| 6 | 10 | 5 | 5 | 50 | 600 |
| 7 | 30 | - | - | 30 | 600 |
| 8 | 30 | 10 | 5 | 150 | 600 |

### 3.3.2 Atmospheric pressure plasma treatment

*Pretreatment*

For the APP trials a colored version of the PET-fabric was used. The properties are the same as for the uncolored one and are described in Table 3. A new approach of applying the chemicals to the fabric was tested, immersing the fabrics in an aqueous dispersion of hydrophobizing agent instead of spraying them (except for the Flexipel products, which were still sprayed on the fabric). The compositions of the different dispersions can be seen in Table 7.

Textile samples were cut out and weighed before being immersed in the dispersion for a couple of minutes, long enough for them to be soaked. They were then calendered by compressing the fabric between two rollers under pressure, 4-6 bar, and weighed again to be able to calculate the absorbed amount of dispersion. A reference sample was made by immersing textile in dispersion number 3, left it to dry over night at room temperature and then cure it in an oven for 1 min at 160 °C.

For a future product, a low pick up of the fluorocarbons is desired hence, in this project different ratios of fluorocarbons were evaluated. Distilled water or mineral spirit was the diluents (fluorocarbon/booster: distilled water/mineral spirit) and one in the concentrated dispersion was evaluated as well. For the cases where booster was included, this was done in an amount of 20 % of the dispersion weight. The pickup was calculated using Eq. 3 or 4.

**Table 7. All the different dispersions and their composition.**

| No. | Chemicals | Amount [g] | Ratio [g chemical/g water] |
|---|---|---|---|
| 1 | AFR6 | 20.3 | 1:100 |
| | EPF 2023 | 5.0 | |
| | Water | 2475 | |
| 2 | AFR6 | 40 | 1:10 |
| | EPF 2023 | 10 | |
| | Water | 400 | |
| 3 | AFR6 | - | - |
| 4 | AFR6 | 20 | - |
| | EPF 2023 | 5 | |
| 5 | AM-95 | 30 | 1:10 |
| | Water | 270 | |
| 6 | S-11 WS | 15 | 1:10 |
| | Mineral spirit | 135 | |
| 7 | AFR6 | 10 | 1:26 |
| | Water | 250 | |
| 8 | AFR6 | 40 | 1:26 |
| | Water | 1000 | |
| 9 | AFR6 | 40 | ~1:20 |
| | EPF 2023 | 10.9 | |
| | Water | 1000 | |
| 10 | AFR6 | 40 | 1:10 |
| | Water | 360 | |

### 3.3.3 APP

*Equipment*

The APP treatments were conducted using a PLATEX 600 LAB made by GRINP, Italy. The major components in the plasma consist of:

- A frame, to which the substrate is mounted.
- Two parallel electrodes (horizontal)
- Water coolant system

- Power supply
- Gas flow regulators

### *Physical parameters*

The equipment has several parameters that can be altered:

- The power (0-6000 W)
- The distance between the two electrodes (1-50mm)
- The speed of the frame
- Number of cycles through the plasma zone
- The process gas
- The gas flow into the space formed between the two electrodes
- The temperature of the electrodes, governed by the water cooling system.

### *Treatment procedure*

Plasma processing was conducted on wet samples (directly after the calendering process), semi-dry samples (that had been left to dry in room temperature for 2 hours) and on samples that had been dried at room temperature over night (completely dry). The plasma treatment was done by mounting the fabric on the frame and then adjusting the gas flow, electrode distance and the speed of the frame. The power can only be adjusted while the plasma is running thus; a certain area of the fabric was kept in the plasmas zone while the power was adjusted was disregarded for further evaluation. After the plasma was stabilized at the desired power level the frame was turned on thus, the fabric was moved through the plasma zone with a predetermined speed. Another approach that was tested was to first plasma treat the textile, then immerse it in the dispersion, calender it and finally leave it to dry in room temperature over night.

The speed of the frame was adjusted on the equipment in arbitrary units and not as specific velocity. The frame speed in m/s was measured for some of the frame speed settings. Four different values of the speed where calculated and a graph was made, Figure 5.

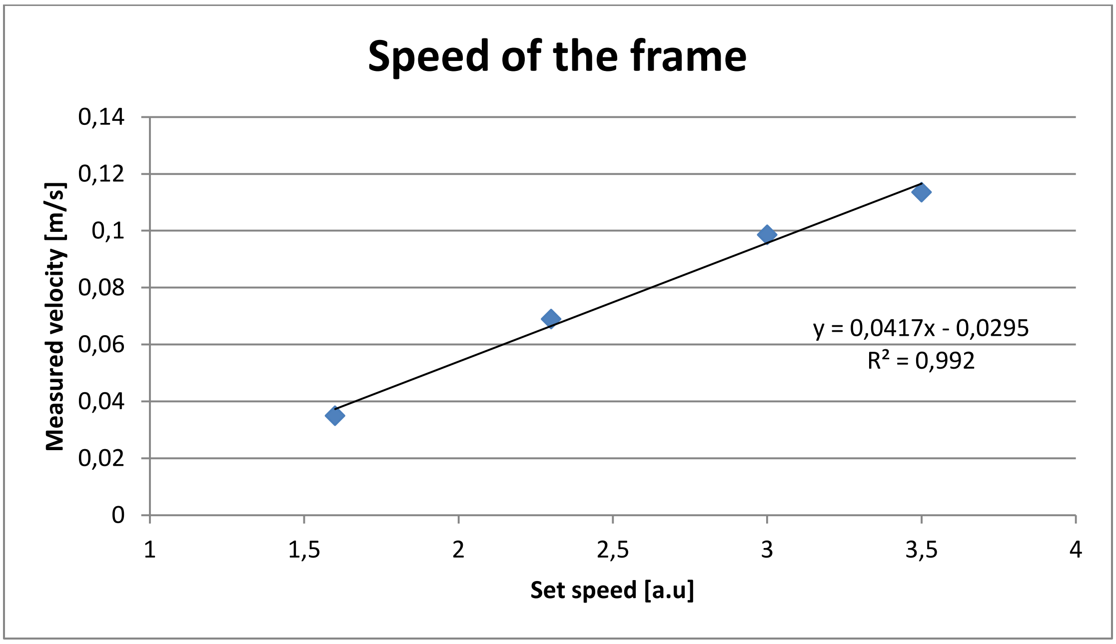


Figure 5 Graph used to determine the speed of the frame from the value presented at the control unit of the plasma.

Several configurations of the plasma parameters were tested. In Table 8 an interval of the different values used for each parameter can be seen. The gas flow and the electrode temperature were kept constant.

**Table 8. The plasma parameters used in the conducted trials.**

| Plasma parameters | |
|---|---|
| Effect | 400 – 4000 W |
| Distance between electrodes | 1-5 mm |
| The speed of the frame | 0.04 – 0.07 m/s |
| Number of cycles | 1-4 |
| Process gas | Helium / Argon |
| Pressure of the gas | 2 bar |
| Gas flow | 7.5 l/min |
| Electrode temperature | 50 °C |

After the plasma treatment the samples were evaluated by measuring the contact angle and the oil and water repellency, both before and after abrasion.

## 3.4 Evaluation of treated samples

*Contact angle measurement*

The static contact angle measurements were performed on a VCA-2500 Video Contact Angle System, from Advanced Surface Technology Inc., using the sessile drop method.

A small sample of the fabric was mounted in the machine and hanging drops of approximately 4-5 µl were made by a micro syringe (Hamilton). The instrument table, on which the substrate was mounted, was raised towards the hanging droplet, which made it adhere to the surface of the substrate. Droplets were placed on three different regions of the substrate and pictures were taken 10 seconds after the droplet had adhered on the surface. The pictures were analyzed by an image analysis program, which calculated the left and right angle of the droplets. The presented contact angle is the arithmetic mean of those two angles. Some of the vacuum-treated samples were analyzed with a different contact angle system at Chalmers University of Technology. The apparatus was a DAT 1100 from Fibro Systems AB, Sweden. Drops with a volume of 4 µl were automatically ejected from the syringe. The contact angle was determined after 10 seconds after the droplet had adhered to the surface by the image analysis software of the instrument.

*Determination of resistance to surface wetting (Spray test) - 24920:1992 SS EN, 4920:1981 ISO*

Equipment

The test was conducted on a spray apparatus (article no 29 60 81) in a room with controlled climate (T= 20 °C, RH = 64%). A sample of 180 x 180 mm was cut from the plasma-treated fabric and mounted on the equipment. 250 ml of distilled water with a temperature of 20 °C was poured into the glass cylinder of the funnel and sprayed on the sample. The sprayed samples were graded from 1-5 where:

1- Wetting of the entire sprayed surface

2- Wetting of half the sprayed surface

3- Wetting of the surface only on small separate areas

4- No wetting, but small drops adheres to the sprayed surface

5- No wetting and no adherence of any drops on the sprayed surface

*Oil repellency – SS- EN ISO 14419:2010*

When testing the oil repellency of a fabric, a modified version of the Swedish Standard SS-EN ISO 14419:2010 was used. The test is conducted by using eight different oils of different surface tensions, where oil number one has the highest surface tension and oil number eight has the lowest (see Table 9)

**Table9. The standard test liquids used with their specific surface tension and density.**

| **Composition** | **Oil test liquid number** | **Density [kg/l]** | **Surface tension [N/m] at 25 ˚C** |
|---|---|---|---|
| Paraffin oil | 1 | 0.84-0.87 | 0.0315 |
| 65 vol%white mineral oil and 35 vol%n-hexadecane | 2 | 0.82 | 0.0296 |
| n-hexadecane | 3 | 0.77 | 0.0273 |
| n-tetradecane | 4 | 0.76 | 0.0264 |
| n-dodecane | 5 | 0.75 | 0.0247 |
| n-decane | 6 | 0.73 | 0.0235 |
| n-octane | 7 | 0.70 | 0.0214 |
| n-heptane | 8 | 0.69 | 0.0198 |

The test was conducted in a room with controlled climate (T = 20 °C, RH = 64%). Samples of approximately 5 x 5 cm was cut from the treated fabric and placed on a white blotting paper. Four to five small drops were carefully placed on the substrate and graded after 30 s, by visual inspection from an angle of approximately 45° from the horizontal plane. The test is started with the lowest-numbered test liquid and proceeds to the next liquid, only if the drops do not penetrate or wet the substrate at the liquid-substrate interface nor if any wicking around the drops does not occur.

The drops on the fabric surface are graded from A-D, where:

A – passes; clear, well-rounded drop

B – borderline pass; rounding drop with partial darkening

C – fails; wicking apparent and/or complete wetting

D – fails; complete wetting

### *Martindale – Abrasion testing*

Samples with a diameter of 38 mm were punch pressed from the fabric, mounted in a specimen holder and rubbed against a standard wool fabric for 2000-5000 cycles, at a load of 12 kPa. The oil repellency was tested before and after this treatment

### *SEM*

SEM was conducted on four specimens by Jan Johansson at Swerea IVF on a Jeol 6610LV.The four specimens were treated in the following way before the measurement:

- An untreated colored PET-fabric
- Reference sample hydrobhobized by FOV fabrics
- Two plasma treated samples (Sample 1, Table 19 - treated with helium and sample 2, Table 19 - treated with argon)

### *ESCA*

ESCA was conducted by Anne Wendel at Chalmers University of Technology. The following samples were tested:

- An untreated PET-fabric.
- A conventionally hydrophobized PET fabric, supplied by FOV fabrics.
- An untreated PET fabric from FOV Fabrics, which had been immersed in 100% AFR6 and plasma-treated (Sample 1 table 19).
- An untreated PET fabric from FOV Fabrics, which had been immersed in 100% AFR6 and left to dry without plasma treatment.

# 4 Results and Discussion

## 4.1 Properties of the reference fabric

*Untreated fabric*

The untreated PET-fabric were evaluated by contact angle measurement as well as oil repellency test. The tests showed that the fabric was hydrophilic; with a contact angle of 0 ° and with liquid number one of the oil repellency test wetting the surface of the fabric.

*The conventionally hydrophobized fabrics*

The hydrophobized fabric from FOV Fabrics was also evaluated. As can be seen in Table 10 the hydrophobized fabric showed a high contact angle as well as an ability to repel test liquid number 1-6.

**Table 10. Results from evaluating an untreated and two conventionally hydrophobized fabrics.**

| **Sample** | **Results** | | | | |
|---|---|---|---|---|---|
| | Average Contact Angle [°] | Oil repellency (Highest liquid passed) | Oil rep. after 2000 cycles in Martindale | Oil rep. after 5000 cycles in Martindale | Spray test grading |
| Untreated PET-fabric | 0 | 0 | - | - | 1 |
| FOV Fabrics Conventionally hydrophobized | 142 | 6 | 2 | 1 | 5 |
| Conventionally hydrophobized at Swerea IVF | - | 7/8 | 2 | - | 5 |

Since the amount of chemicals used in the hydrophobized fabric from FOV was lower than the amount used in dispersion number 3, which was the main chemical bath evaluated. A sample was hydrophobized in a  conventional way, without plasma treatment, at Swerea IVF and used as reference. The evaluated properties of this sample can also be seen in Table 10. It showed high oil- and water repellency.

## 4.2 Vacuum plasma

Eight unique set of plasma parameters were evaluated, and even though all those treatments are reported in the appendix, only the samples that showed a hydrophobic character will be presented in the results below. Initial trials were made with the vacuum plasma to help find optimal parameters for the APP. The result of the vacuum plasma treatment was mainly evaluated by contact angle measurements, but oil repellency was also tested in some cases.

*Untreated polyester*

A hydrophobic effect was achieved for the majority of the treated samples, as illustrated by a contact ange > 90°. The exception being for the 10s and 30s treated samples at 300 W where the time in the plasma zone or the power was insufficient for enough fluorine atoms/molecules to adhere to the fabric surface. When comparing the 300 W and 600 W (Figure 6) the contact angles are similar except for the sample that was cycled 5 times for 30s at 600 W, which gave a lower contact angle. The reason for this might be due to an etching effect from the high energy input and extensive residence time in the plasma zone. Hence, there seem to be optimum plasma parameters in each case, where the desired effect is lowered upon extended plasma treatment.

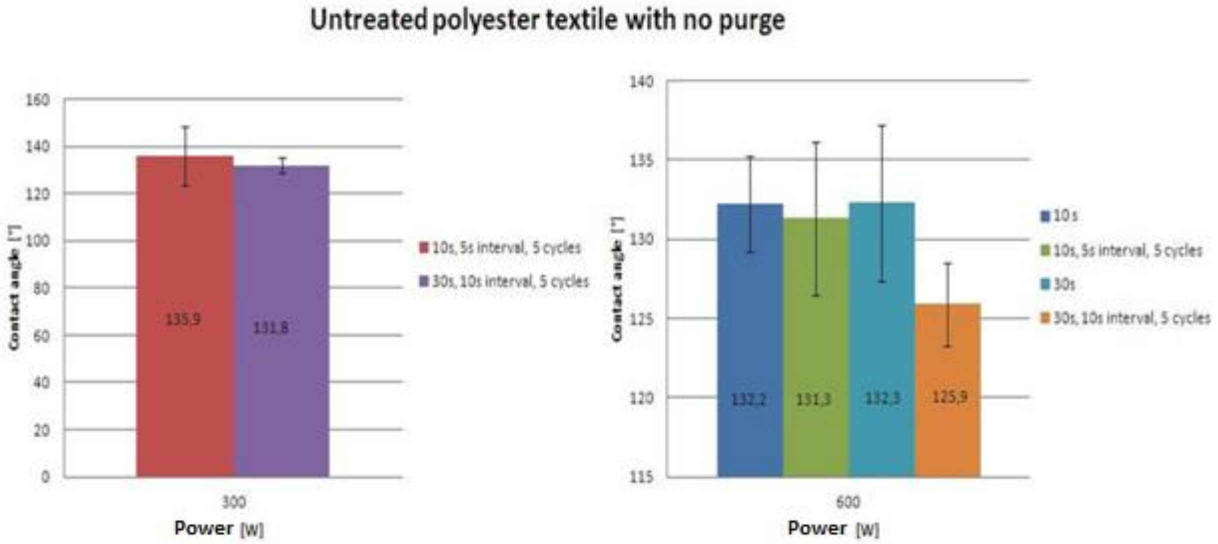


Figure 6 Contact angles of the non-pretreated/vacuum plasma treated PET-fabric. Left: Treated at 300 W. Right: Treated at 600 W

*Wet samples*

As can be seen in Figure 7, two of the fabrics treated at 300 W and three of the fabrics treated at 600 W showed hydrophobic properties. The average value of the contact angle of the samples treated at the higher power was somewhat higher than the samples treated at lower power and there seems to be a minimum time needed in the plasma zone to obtain a certain degree of hydrobobization. The results are surprising however, since the fabrics were completely water-soaked when placed inside the plasma chamber. A hypothesis is that the low working pressure of the plasma vaporizes most of the water content to such a degree that the water content will not Influence the results.

What should also be mentioned is that although the 600 W, 30s , cycled sample had the lowest contact angle it still showed the best hydrophobic properties when the contact angle measurement was conducted. The drop was reluctant to leave the syringe for the substrate and a bit of force was needed to make it adhere to the surface of the fabric. The reason for this might be that the properties of the fabric are inhomogeneous, with certain areas being hydrophobic while some are hydrophilic.

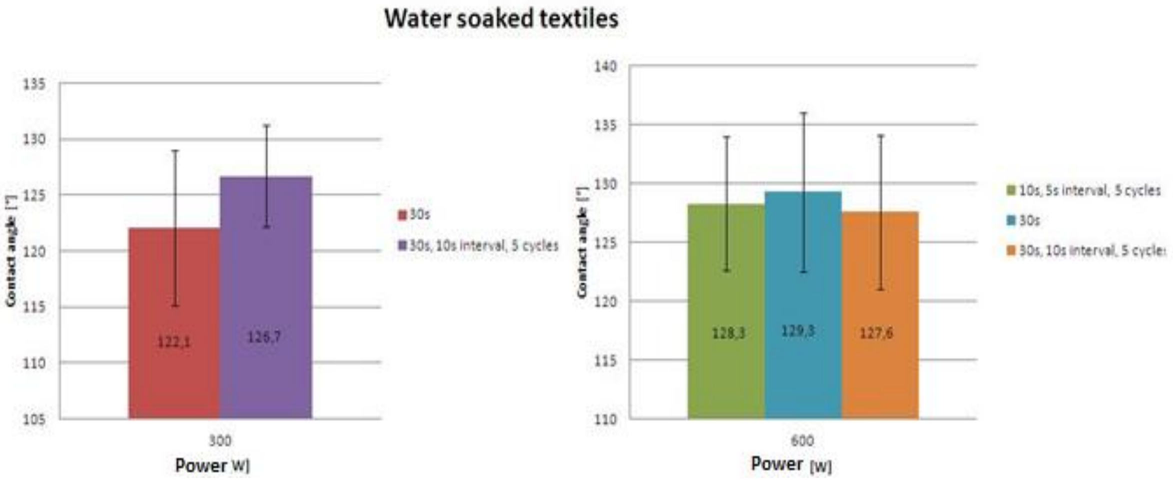


Figure 7 Contact angles of water soaked/ vacuum plasma treated PET-fabrics. Left: Treated at 300 W. Right: Treated at 600 W

*Samples where the air has been purged through the vacuum chamber of the plasma*

The textiles treated for 10 seconds, for both at 300 W and 600 W showed no hydrophobic properties, as can be seen in Figure 8. Also, the samples treated at a higher power showed generally higher contact angles and lower standard deviations. However, the 30 second sample treated at 600 W proved to be dynamic, with an apparent decrease of the contact angle with time.

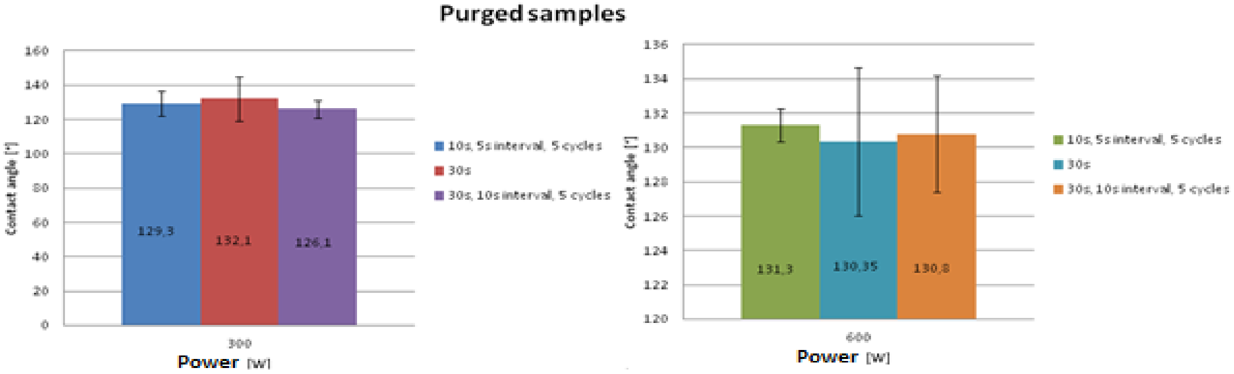


Figure 8 Contact angles of purged/ vacuum plasma treated PET-fabrics. Left: Treated at 300 W. Right: Treated at 600 W

*Dried and purged samples*

For the pre-dried and purged samples ,Figure 9, all cycled samples showed high contact angles as well as the 30s sample at 600 W. All other samples were hydrophilic, where a hydrophobic character occurred for a very limited time after application of the drop. Short runtimes without cycles has worked on previous samples (for instance for the untreated polyester fabric above), but for some reason it does not work for the dried and purged samples. The dried and purged samples also showed the overall lowest values of the contact angles compared to the previous samples above (figure 6, 7 and 8).

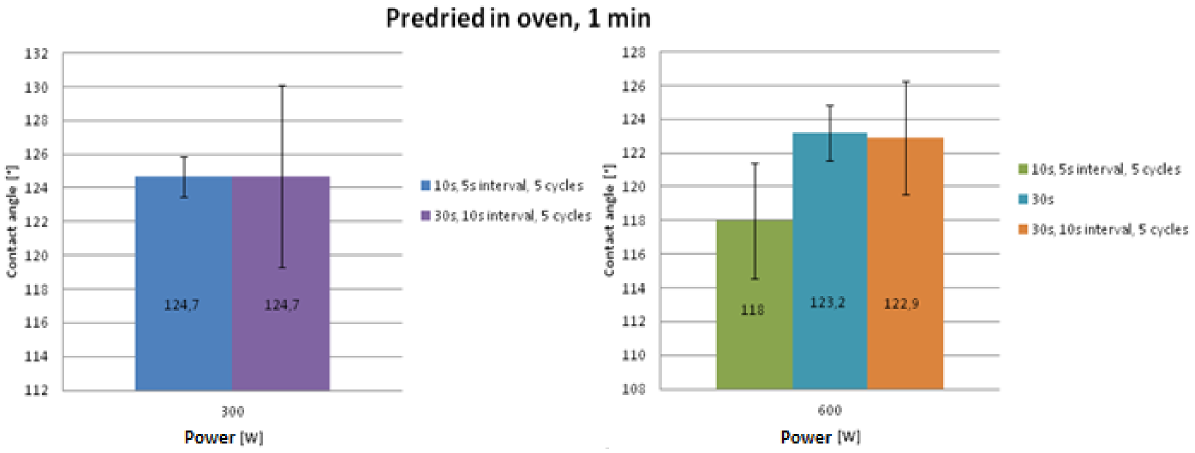


**Figure 9 Contact angles of pre-dried / vacuum plasma treated PET-fabrics. Left: Treated at 300 W. Right: Treated at 600 W**

*RUCO-GUARD® AFR6 and RUCCO-GUARD® EPF 2023*

Figure 10 shows the results for the pre-dried (1min at 100 °C); AFR6/booster treated and cured for one minute samples. All samples showed hydrophobic properties. The 600 W samples showed higher average contact angles but all drops remained unchanged on the substrate. The contact angle measurement of the cycled 30 s sample at 600 W was performed on an automated machine at Chalmers University of Technology. The contact angles were similar to the reference sample which had only been dried, cured and not plasma treated. The sample with the highest contact angle was the one that was treated for 10s at 600 W.

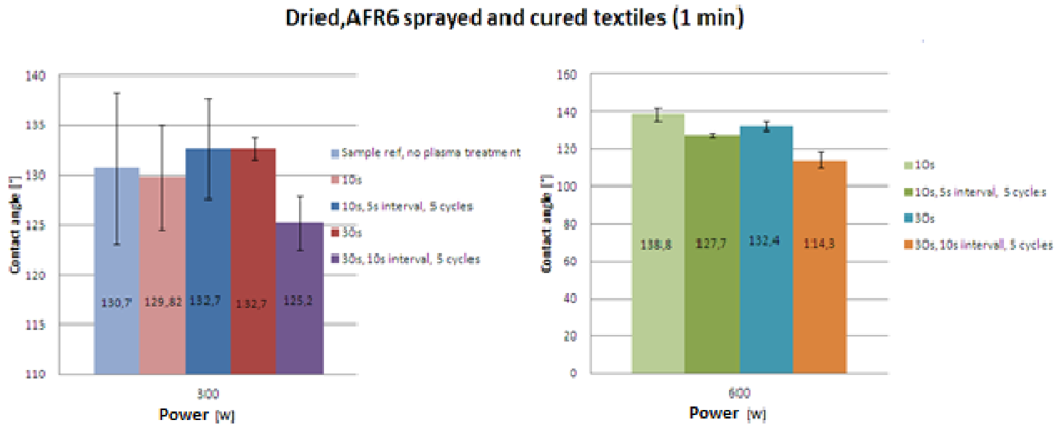


Figure 10 Contact angles of pre-dried, AFR6/EPF 2023 sprayed, cured (1 min) and vacuum plasma treated PET-fabrics. Left: Treated at 300 W. Right: Treated at 600 W

All samples that were pre-dried, sprayed with AFR6/Booster and cured for 1 min before the plasma treatment showed hydrophobic properties, Figure 11. The reference sample however was not hydrophobic. The values of the contact angle were similar for both the high and low effect treated samples.

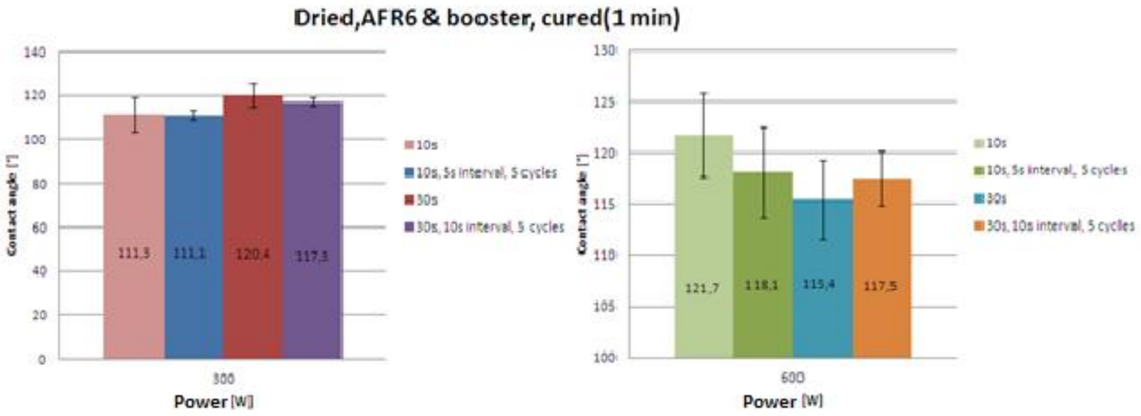
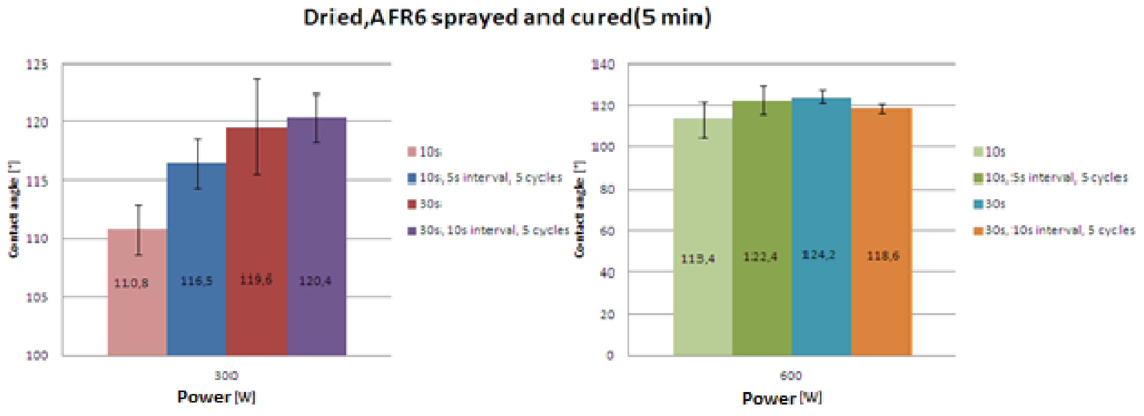


Figure 11 Contact angles of pre-dried, AFR6/EPF 2023 sprayed and vacuum plasma treated PET-fabrics. Left: Treated at 300 W. Right: Treated at 600 W

Samples that were treated in the same way as above, but cured for 5 minutes instead of 1 min, showed the following contact angles (Figure 12).



Figuer 12 Contact angles of pre-dried, AFR6 sprayed, cured (5 min) and vacuum plasma treated PET-fabrics. Left: Treated at 300 W. Right: Treated at 600 W

All samples proved to be hydrophobic except for the reference sample (which is not presented in the figure). The contact angles are generally lower than for the two earlier measurements which had been cured for 1 min. This was probably due to the changed apparatus as well as procedure of measuring the contact angle. However, the specific chemicals used, along with the curing and plasma treatment seem to ensure hydrophobic properties of the fabric.

When using argon as the process gas for the samples that were pre-dried, AFR6 sprayed and cured for 1 min, only three samples showed hydrophobic properties, Figure 13. Compared to the reference sample which was not plasma treated, the values of the contact angles were significantly reduced which is most likely caused due to the dominating etching mechanism of the plasma, which remove some of the hydrophobizing chemicals from the fabric surface..

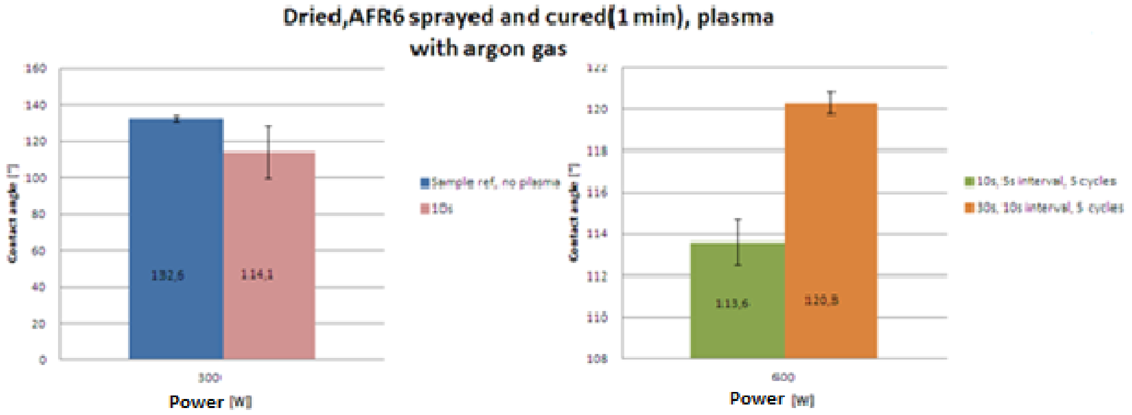


Figure 13 Contact angles of pre-dried, AFR6 sprayed and argon vacuum plasma treated PET-fabrics. Left: Treated at 300 W. Right: Treated at 600 W

The contact angles for the samples that were dried, sprayed with AFR6 and plasma treated, but not cured with heat are illustrated in Figure 14). For the samples plasma-treated at 300 W, only the cycled 30s sample was hydrophobic. All samples treated at 600 W were hydrophobic.

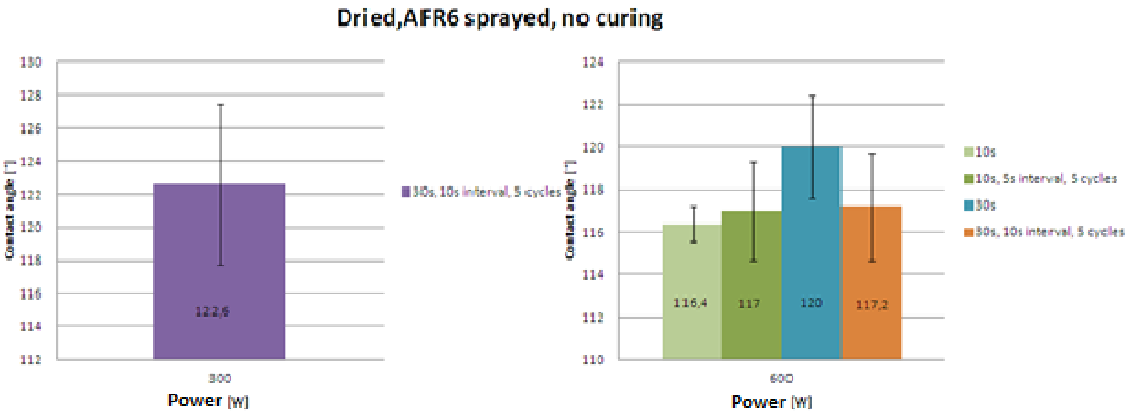


**Figure 14 Contact angles of pre-dried, AFR6 sprayed and vacuum plasma treated PET-fabrics. Left: Treated at 300 W. Right: Treated at 600 W**

*Further trials with vaccum plasma using dispersion No. 3*

Further trials using the vacuum plasma were conducted to see if better results were achievable using chemical bath No.3 which had shown promising results with the APP. The results of the contact angles measurement can be seen in Figure 15 (which was performed with Swerea IVFs apparatus). All samples showed hydrophobic properties except for the reference sample and the sample treated for 10s at 600 W. The highest contact angle measured was for the sample treated for 30s at 400 W.

When comparing the contact angles with the results from the oil repellency (Table 11) it is clear from the results that the contact angle is sometimes a misleading measure of the hydrophobicity of plasma-treated samples. The reason for this is probably due to that the fiber surface is uneven which makes it difficult to obtain a representative value of the contact angle. Therefore, soley measuring the contact angle is not sufficient in determining the hydrophobicity of textiles. The vacuum-treated sample at 600 W was wetted by the water drops during measurement of the contact angle, but showed great oil repellency. The effect of the plasma treatment is also significant when comparing with the reference sample which is only able to repel the first test liquid while the best of the vacuum treated samples are able to repel oils of up to test liquid 5.

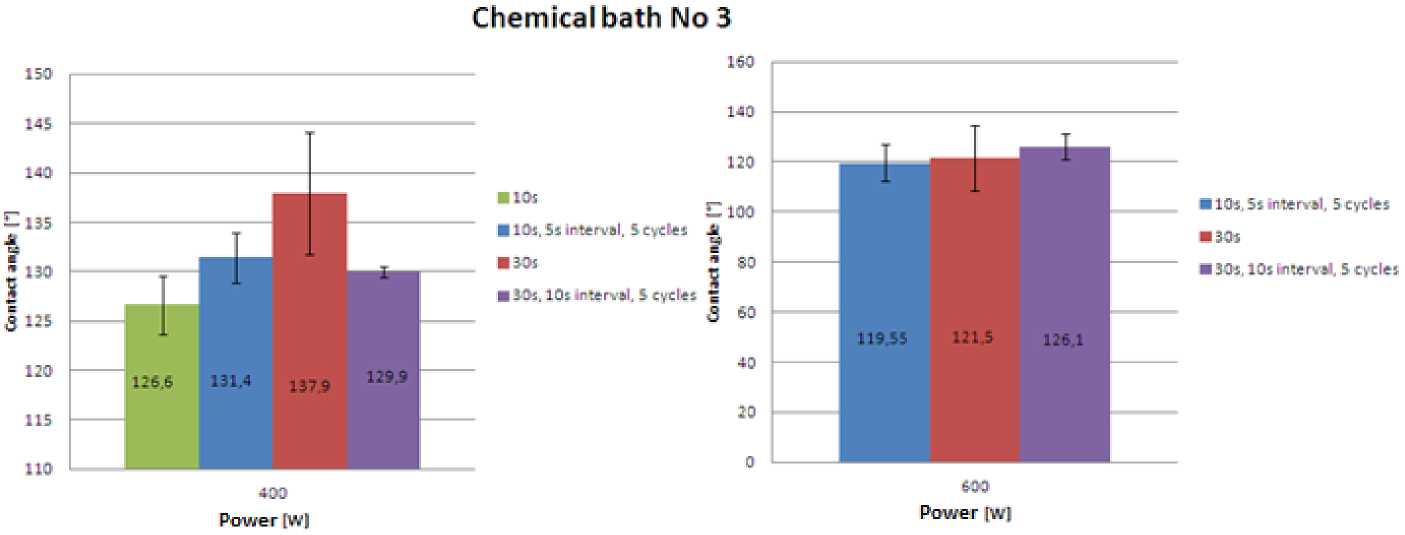


Figure 15 Contact angles of Chemical bath No.3 / vacuum plasma treated PET-fabrics. Left: Treated at 300 W. Right: Treated at 600 W

**Table 11. Oil repellency for samples immersed in dispersion No.3 and vacuum plasma treated with $CF_4$.**

| Power | Sample | Test liquid | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| | Reference | A | B | C | D | D | | | |
| 400 W | 10s | | | | A | B | D | | |
| | 10 s,5 cycl | | | | A | B | C | | |
| | 30s | | | A | B | B | C | | |
| | 30s, 5 cycl | | B | B | D | D | | | |
| 600 W | 10s | | | | B | B | C | | |
| | 10s, 5 cycl | | | | B | B | D | | |
| | 30s | | A | B | D | D | | | |
| | 30s, 5 cycl | | A | B | D | D | | | |

In Table 11 the results of the oil repellency tests can be seen (A-B: Oil repellency passed for the specific liquid, C-D: Oil repellency failed for the specific liquid) for dispersion No.3. The best results can be seen for the samples that were in the plasma zone for a shorter time (10s with and without any cycling) where some were able to repel up to liquid 5. The power of the plasma does not seem to be a determining parameter to achieve good oil repellency. It should be mentioned though that the effect of a longer treatment time in the plasma zone did not diminish the oil repellency compared to the reference sample. Instead a small increase can be seen, where the plasma treated samples are now able to repel up to liquid 3 whilst the reference was only able to repel liquid 2.

## 4.3 APP

The results presented below will only include APP trials with the concentrated bath of the AFR6 (dispersion No.3), Flexipel AM-95 (dispersion No. 5) and Flexipel S-11 WS (dispersion No.6) because these showed the most promising results of a large amount of trials. The results from all the other trials can be found in the appendix.

### AFR6 (dispersion No.3)

In Table 12 results are presented for wet ( that are immersed, and plasma treated directly after being calendered)  dry (same procedure as for the wet samples but are left to dry in R.T over night) and samples that have been plasma treated prior to being exposed to the dispersion. The samples have been run through the plasma zone with power from 1200 to 2000 W, a speed of the frame of 2.5 with 4 cycles. The electrode distance was between 3 and 5 mm.

The results for the wet samples show hydrophobic contact angles for all samples (they exceed 90 °) with sample 8 showing the highest contact angle of 141.5 °.  The contact angles can however not be directly related to the oil repellency of the fabric, but merely be used as a screening test of the hydrophobic properties. This is seen in i.e. sample 1 which shows the lowest contact angle of table.12 but still has a greater oil repellency than sample 2 and 3.

The best oil repellency for the wet samples that are plasma treated directly after being calendered can be seen for the samples 5-8 which all have in common an increased energy input compared to the first three samples.

**Table 12. Parameters and results for differently treated samples. The speed of the frame was 2.5 and with 4 cycles through the plasma zone.**

| **Wet samples** | | | | |
|---|---|---|---|---|
| **Sample** | **Plasma parameters** | | **Results** | |
| | **Power [W]** | **Distance between electrodes [mm]** | **Average Contact Angle [°]** | **Oil repellency (Highest liquid passed)** |
| **1** | 1200 | 3 | 98,1 | 6 |
| **2** | 1200 | 4 | 123,4 | 5 |
| **3** | 1200 | 5 | 129,3 | 5 |
| **4** | 1600 | 3 | 137,6 | 7 / 8 |
| **5** | 1600 | 4 | 103,0 | 7 / 8 |
| **6** | 1600 | 5 | 135,8 | 7 / 8 |
| **7** | 2000 | 3 | 136,1 | 7 / 8 |
| **8** | 2000 | 4 | 141,5 | 7 / 8 |
| Dry samples | | | | |
| | **Power [W]** | **Oil repellency (Highest liquid passed)** | **Average Contact Angle [°]** | **Oil repellency (Highest liquid passed)** |
| **9** | 1200 | 3 | 133,7 | 6 |
| **10** | 1200 | 4 | 135,5 | 6/7 |
| **11** | 1200 | 5 | 137,9 | 6/7 |
| **12** | 1600 | 3 | 134,1 | 7/8 |
| **13** | 1600 | 4 | 134,1 | 6/7 |
| **14** | 1600 | 5 | 135,9 | 6/7 |
| **15** | 2000 | 3 | 132,1 | 7 |
| **16** | 2000 | 4 | 138,3 | 7 |
| **17** | 2000 | 5 | 129,4 | 6 |
| Plasma treated and then exposed to dispersion No 3 | | | | |
| | **Power [W]** | **Distance between electrodes [mm]** | **Average Contact Angle [°]** | **Oil repellency (Highest liquid passed)** |
| **18** | 1200 | 3 | 109,1 | 2 |
| **19** | 1200 | 4 | 113,5 | 3 |
| **20** | 1200 | 5 | 118,1 | 3 |
| **21** | 1600 | 3 | 102,5 | 3 |
| **22** | 1600 | 4 | 116,4 | 3/4 |
| **23** | 1600 | 5 | 109,2 | 3 |
| **24** | 2000 | 3 | 119,2 | 3/4 |
| **25** | 2000 | 4 | 116,7 | 3/4 |
| **26** | 2000 | 5 | 113,4 | 3/4 |

The dry samples in Table 12 were plasma treated in the same way as the wet samples but with the difference that they were completely dry before being run through the plasma zone. All samples showed high contact angles and an overall higher oil repellency. However, sample 12 was the only sample that had the ability to repel liquids between 7 and 8 while the wet samples that had been plasma treated directly after being calendered had five samples with this ability.

According to Table 12, the samples that were plasma-treated prior to the exposure to the dispersion appeared to give least hydrophobic properties, compared to the other methods. However, the contact angles for all samples in table 12 are well above $90^o$, i.e. the surfaces are all hydrophobic, and the oil repellencies are still higher than for an untreated fabric (see Table 13, reference sample). The reason for these results may be due to the fact that the specific chemical used needs some sort of energy input after the wet impregnation of the fabric to achieve an activation of the fluorocarbons thus making the molecules “stand up” on the surface.

In Table 13 the samples have been run through the plasma zone with a lower speed (1.9) and with a changed electrode distance (2-4 mm). Decreasing the electrode distance leads to a more homogenous plasma field and thus a more homogenous treatment of the fabric.

The results in Table 13 show that the contact angles for all the wet samples that had been plasma treated directly after being calendered are hydrophobic except for a reference sample which was not plasma treated. Since it has been shown that a contact angle above 90° is no guarantee for a fabric’s ability to repel oils according to the oil repellency test, describe earlier. The contact angle measurements are merely used as a screening test, to set the correct plasma parameters and are not analyzed further, or reported within this context.

If the degree of oil repellency in the previously wet samples were solely dependent on the plasma power, the samples in Table 13 show that the plasma power is only one part of the equation, since both the highest and the lowest oil repellency can be seen for the samples exposed to the highest plasma power

What should also be noticed is the apparent effect of the plasma; the oil repellency increases from only being able to repel liquid 2 with only the chemical to almost repel liquid 8 after being treated with the plasma.

**Table 13. Parameters and results for differently treated samples. The speed of the frame was 1.9 and with 4 cycles through the plasma zone.**

| Wet samples | | | | |
|---|---|---|---|---|
| **Sample** | **Plasma parameters** | | | **Results** |
| | **Power [W]** | **Distance between electrodes [mm]** | **Average Contact Angle [°]** | **Oil repellency (Highest liquid passed)** |
| Reference | - | - | 67,0 | 2 |
| 1 | 1200 | 2 | 117,3 | 6 |
| 2 | 1200 | 3 | 133,1 | 6 |
| 3 | 1200 | 4 | 124,1 | 6 |
| 4 | 1600 | 2 | 111,3 | 6 |
| 5 | 1600 | 3 | 132,6 | 7 |
| 6 | 1600 | 4 | 131,2 | 7 / 8 |
| 7 | 2000 | 2 | 112,1 | 5 |
| 8 | 2000 | 3 | 104,7 | 7 / 8 |
| 9 | 2000 | 4 | 130,3 | 6 |
| **Dry samples** | | | | |
| | **Power [W]** | **Distance between electordes [mm]** | **Average Contact Angle [°]** | **Oil repellency (Highest liquid passed)** |
| 10 | 1200 | 2 | 135,8 | 7 |
| 11 | 1200 | 3 | 142,8 | 7/8 |
| 12 | 1200 | 4 | 143,4 | 7/8 |
| 13 | 1600 | 2 | 125,0 | 7/8 |
| 14 | 1600 | 3 | 133,7 | 7/8 |
| 15 | 1600 | 4 | 138,3 | 7/8 |
| 16 | 2000 | 2 | 131,3 | 7 |
| 17 | 2000 | 3 | 131,2 | 7/8 |
| **Plasma treated and then exposed to chemical** | | | | |
| | **Power [W]** | **Distance between electrodes [mm]** | **Average Contact Angle [°]** | **Oil repellency (Highest liquid passed)** |
| 18 | 1200 | 2 | 119,8 | 3/4 |
| 19 | 1200 | 3 | 103,3 | 3/4 |
| 20 | 1200 | 4 | 113,5 | 3/4 |
| 21 | 1600 | 2 | 109,9 | 3/4 |
| 22 | 1600 | 3 | 110,6 | 3/4 |
| 23 | 1600 | 4 | 118,5 | 3 |
| 24 | 2000 | 2 | 131,1 | 3/4 |
| 25 | 2000 | 3 | 115,1 | 3/4 |
| 26 | 2000 | 4 | 114,9 | 3/4 |

For the dry samples in Table 13 all contact angles are high and the oil repellency is the overall highest compared to the APP trials so far described, with an oil repellency of 7 or higher. At this speed through the plasma zone, the difference in power and distance between the electrodes appears not to be the determining parameters to achieve a high level of oil repellency.

The samples that were plasma-treated prior to being exposed to dispersion No 3 still showed poor results and the reason for this, as stated previously, is most likely due to the need of an energy input to fixate the fluorocarbons on the surface of the fabric. Hence, plasma activation of the surface is not sufficient and an additional plasma treatment of these fabrics would be needed.

After these trials it became apparent that the main focus should be on plasma treatment of dry samples since they were the ones showing the most promising results. The parameters of sample 12 and 13 from Table 13 were therefore further evaluated to see how the oil repellency was affected by abrasion testing using a Martindale apparatus. The results can be seen in Table 14.

**Table 14. Further evaluation of dry samples and also reference samples – oil repellency after 5000 cycles against wool fabric with a load of 12kPa in Martindale apparatus.**

| Sample | Plasma parameters | | | | Resultat | | |
|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) | Oil rep. after 5000 cycles in Martindale (Highest liquid passed) |
| Untreated PET-fabric | - | - | - | - | 0 | 0 | - |
| FOV Fabrics Conventionally hydrophobized | - | - | - | - | 142 | 6 | 1 |
| Conventionally hydrophobized at Swerea IVF | - | - | - | - | - | 7/8 | 1 |
| 1 | 1200 | 1.9 | 4 | 4 | 135,3 | 7 | 1 |
| 2 | 1600 | 1.9 | 2 | 4 | 138,1 | 7 | 1 |

The abrasion testing of the fabric is a very rough treatment; this was clearly noticed by visual inspection of the fabric.. The color had faded and the textile had become fuzzier. Even so, the plasma-treated fabric still maintained a certain degree of oil repellency, according to Table 14.

An attempt to increase the hydrophobicity by rinsing the plasma-treated fabrics with distilled water was also tested. The reason for this is to remove any of the surfactants which might have accumulated on the fabric surface from the dispersion. Such adsorbed surfactants provide wetting of the surface and hence, impair the hydrophobic properties of the textile, but could be desorbed by water. The samples were evaluated after they had dried in room temperature over night.

The results can be seen in Table 15, showing no significant improvement of the hydrophobicity compared to samples that were not rinsed with water. The oil repellencies are more or less the same as before rinsing with water (see Table 14).

**Table 15. Three samples that had been rinsed with distilled water after the plasma treatment.**

| Sample | Plasma parameters | | | | Results | | |
|---|---|---|---|---|---|---|---|
| | Effect [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) | Spray test grading |
| 1 | 1200 | 1.9 | 4 | 4 | 135,7 | 6 | 1 |
| 2 | 1600 | 1.9 | 2 | 4 | 138,9 | 6/7 | 1 |
| 3 | 2000 | 2.5 | 3 | 4 | 134,7 | 7/8 | 1 |

Also a spray test was conducted to see how well the fabric repelled large quantities of water. The test showed poor results with a grading of 1. A light microscope was used to check if the samples had been damaged by the plasma treatment. This was not the case for sample 1 and 2 but sample 3 which had been treated with a fairly high power showed some pinholes that most likely had arisen due to discharges in the plasma.

There are two ways to ensure a homogenous plasma zone:

1. By applying a sufficient amount of energy
2. Lowering the distance between the electrodes
3. Selection of process gas

Since the helium had worked well so far and that both nitrogen and argon gave inhomogeneous plasma zones, the parameters that were altered to obtain a more homogenous plasma zone were the electrode distance and the power of the plasma.

In Table 16 two samples were treated with a higher power (3000 W) and a lower distance between the electrodes (1 mm) to ensure that no discharges would occur that could damage the fabric. Sample 1 was run once and sample 2 was run four times through the plasma zone. These samples were also rinsed by distilled water after the plasma treatment and were left to dry in R.T. before further evaluation.

**Table 16. Plasma treatment with high powers and a small distance between the electrodes. Samples were rinsed with distilled water after plasma treatment.**

| Sample | Plasma parameters | | | | Results | | | |
|---|---|---|---|---|---|---|---|---|
| | Power[W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) | Oil rep. after 2000 cycles in Martindale | Spray test grading |
| **1** | 3000 | 2.5 | 1 | 1 | 132,7 | 6 | - | 1 |
| **2** | 3000 | 2.5 | 1 | 4 | 131,0 | 6 | 3/4 | 1 |

When studying the fabrics from Table 16 in a light microscope no damage could be seen. Thus operating at lower electrode distances is more ideal. The results from the oil repellency test showed that both samples were able to repel test liquid number 6. The oil repellency differed however after a Martindale treatment of 2000 cycles where sample 1 which had not been cycled in the plasma showed no oil repellency while sample two which had been run through the plasma zone four times was still able to repel test liquid number 4. This is probably due to a stronger binding of the chemicals to the substrate caused by the longer residence time in the plasma zone. The results of the water spray test showed poor results for both samples.

Next the result of different number of cycles (1-3) through the plasma zone was evaluated. This was done by treating 9 new samples with powers ranging from 1200 W – 2000 W, 1 mm in distance between the electrodes (to assure no damage was made to the fabric) and with 2.5 being the speed of the frame. The samples were rinsed with distilled water after the plasma treatment and the results can be seen in Table 17.

**Table 17. Plasma parameters and the results from different amount of cycles through the plasma zone.**

| Sample | Plasma parameters | | | | Results | | | |
|---|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) | Oil rep. after 2000 cycles in Martindale | Spray test grading |
| 1 | 1200 | 2.5 | 1 | 1 | 137,1 | 7/8 | 4 | 1 |
| 2 | 1200 | 2.5 | 1 | 2 | 138,8 | 7 | 4 | 1 |
| 3 | 1200 | 2.5 | 1 | 3 | 137,9 | 7 | 3/4 | 1 |
| 4 | 1600 | 2.5 | 1 | 1 | 138,0 | 7/8 | 3/4 | 1 |
| 5 | 1600 | 2.5 | 1 | 2 | 139,7 | 7/8 | 4 | 1 |
| 6 | 1600 | 2.5 | 1 | 3 | 140,4 | 6/7 | 4 | 1 |
| 7 | 2000 | 2.5 | 1 | 1 | 139,3 | 7/8 | 4 | 1 |
| 8 | 2000 | 2.5 | 1 | 2 | 135,2 | 7 | 4 | 1 |
| 9 | 2000 | 2.5 | 1 | 3 | 138,7 | 6/7 | 4 | 1 |

These results show great oil repellency for all samples which was not expected, a substantial trend cannot be seen between the oil repellency and number of cycles. Even after the abrasion testing the oil repellency results are similar. The water spray tests still show poor results.

A new batch of the AFR6 dispersion was received from Rudolph GmbH to do further test on the fabric, including determination of the pickup of the chemical on the textile. Three new samples were tested, one that was a reference sample that was immersed in the dispersion and not plasma-treated and two samples that were treated according to Table 18.

**Table 18. Plasma parameters, pickup and results from a reference (that was treated with the same chemical but was not plasma treated) and two plasma treated samples.**

| Sample | Plasma parameters | Results | | | | | |
|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Pickup [%] | Oil repellency (Highest liquid passed) | Spray test grading |
| Reference | - | - | - | - | 54,5 | 3 | 1 |
| 1 | 1600 | 2.5 | 1 | 3 | 53,3 | 5 | 1 |
| 2 | 1600 | 2.5 | 1 | 4 | 53,9 | 5 | 1 |

The results showed a decrease in oil repellency compared to the samples in Table 17, which were treated in the same way. Hence, the chemicals in the new batch seem to have interacted differently than those in the previous batch. This is also seen for the reference sample, which for this latter batch shows higher oil repellency than the reference sample in Table 13. The pickup of the dispersion is approximately 54% and the samples were graded as a 1 in the water spray test. The treatment was repeated, giving the same results.

Also argon was tested as a process gas, instead of helium. The results are shown in Table 19. It is clear that argon works well for this application, as seen by the good results from the oil repellency test.

**Table 19. Plasma parameters and results for 8 new samples that were plasma treated either with argon or helium gas. All samples were cycled 4 times.**

| Sample | Plasma parameters | | | | Results | |
|---|---|---|---|---|---|---|
| | Effect [W] | Speed of the frame | Distance between electrodes [mm] | Process gas | Pickup [%] | Oil repellency (Highest liquid passed) |
| **1** | 1600 | 2.5 | 1 | Helium | 45,7 | 5 |
| | | | | Argon | 48,2 | 6/7 |
| **2** | 1600 | 2.5 | 2 | Helium | 44,6 | 6 |
| | | | | Argon | 47,0 | 8 |
| **3** | 2000 | 2.5 | 1 | Helium | 45,9 | 5 |
| | | | | Argon | 46,4 | 6/7 |
| **4** | 2000 | 2.5 | 3 | Helium | 45,9 | 7 |
| | | | | Argon | 46,5 | 6 |

The oil repellency increased with increasing the distance between the electrodes when comparing the helium treated samples with each other. A smaller distance between the electrodes might give rise to a rougher treatment of the fabric surface (higher energy input) which then results in a disintegration instead of crosslinking of the fluoro-polymers on the surface. Thus, finding the optimal parameters for each sample is crucial. The optimal electrode distance when using argon as the process gas is 2 mm which also resulted in the highest oil repellency of all the samples (it was able to repel liquid 8)..

After these promising results, further trials were conducted using argon as the process gas instead of helium. The parameters and results from these trials can be seen in Table 20.

**Table 20. Parameters and results for 6 new samples which were all plasma-treated with argon gas.**

| **Sample** | **Plasma parameters** | | | | **Results** | | | |
|---|---|---|---|---|---|---|---|---|
| | **Power [W]** | **Speed of the frame** | **Distance between electrodes [mm]** | **No. of cycles** | **Pickup [%]** | **Oil repellency (Highest liquid passed)** | **Oil rep. after 2000 cycles in Martin dale** | **Spray test grading** |
| 1 | 1600 | 2.5 | 1 | 4 | 45,0 | 6 | 3 | 1 |
| 2 | 1600 | 2.5 | 2 | 4 | 45,6 | 7 | 3 | 1 |
| 3 | 1600 | 2.5 | 3 | 4 | 45,4 | 6 | 2 | 2 |
| 4 | 1600 | 2.5 | 4 | 4 | 46,5 | 6/7 | 2 | 2 |
| 5 | 2000 | 2.5 | 3 | 4 | 46,9 | 7 | 3/4 | 2 |
| 6 | 2000 | 2.5 | 4 | 4 | 46,0 | 7/8 | 3/4 | 3 |

The results show high oil repellencies for all samples, where sample 6 stands out as the best and also was graded highest in the spray test. The effect of the hydrophobization was also still present for all samples even after 2000 cycles in the Martindale apparatus.

### Flexipel AM-95 (Dispersion No.5)

These samples were not immersed but sprayed with a dispersion of Flexipel AM-95 in distilled water, no pickup was measured for these samples. The samples were sprayed with the dispersion and left to dry in a fume hood for three days before being plasma treated and evaluated. Table 21 shows the plasma parameters and the results from these trials.

**Table 21. Plasma parameters and results for a reference sample (that was sprayed with the chemical but not plasma treated) and two plasma-treated PET-fabrics.**

| **Sample** | **Plasma parameters** | | | | **Results** | |
|---|---|---|---|---|---|---|
| | **Power [W]** | **Speed of the frame** | **Distance between electrodes [mm]** | **No. of cycles** | **Average Contact Angle [°]** | **Oil repellency (Highest liquid passed)** |
| Reference | - | - | - | - | 139,5 | 8 |
| 1 | 1600 | 2.5 | 1 | 2 | 118,3 | 6 |
| 2 | 1600 | 2.5 | 1 | 3 | 123,9 | 6 |

The results from the table above show that Flexipel AM-95 works better without any form of plasma treatment. Both the contact angles and the oil repellency shows greater values for the reference sample than for the plasma treated ones.

The drying time was longer than for the other dispersions and further evaluation of dispersion No 5 was made to see if it was possible that the long drying time of the fabric might have had a bad impact on the results before plasma treating it. So instead of letting it dry for 3 days at R.T. the samples were left to dry over night, before plasma treatment.

Another test was also made to see if the chemicals could be bound harder to the substrate by first plasma treating the fabric and then spray it with the dispersion and evaluate the oil-repellency before and after a Martindale treatment and compare the results to a reference sample that had been sprayed with the same dispersion but not plasma treated. Table 23 shows the plasma parameters and results from these trials, where sample 1 was sprayed before the plasma treatment and sample 2 after the plasma treatment.

**Table 23. Plasma parameters and results for a reference sample (sprayed with the dispersion No 5 but not plasma treated) and two plasma treated samples.**

| **Sample** | **Plasma parameters** | | | | **Results** | | |
|---|---|---|---|---|---|---|---|
| | **Power [W]** | **Speed of the frame** | **Distance between electrodes [mm]** | **No. of cycles** | **Average Contact Angle [°]** | **Oil repellency (Highest liquid passed)** | **Oil rep. after 2000 cycles in Martindale** |
| Reference | - | - | - | - | 139,4 | 8 | 4/5 |
| 1 | 1600 | 2.5 | 1 | 3 | 108,4 | 6 | 4 |
| 2 | 1600 | 2.5 | 1 | 3 | 141,2 | 8 | 4/5 |

As can be seen from the results the reduced drying time of the chemical had no effect on the result. The plasma treatment prior to the chemical exposure did not either show any difference in oil repellency after 2000 cycles in the Martindale apparatus, between the reference sample and the plasma-treated counterpart.

### Flexipel S-11 WS (DispersionNo.6)

These samples were not immersed but sprayed with a dispersion of Flexipel S-11 WS in odorless mineral spirit. Table 23 shows the plasma parameters as well as the results from these trials. One sample worked as a reference and was not plasma-treated, another sample was sprayed and then plasma treated and a final sample was plasma treated before being sprayed with the dispersion.

**Table 23. Plasma parameters and results for a reference sample, sample 1 was sprayed and plasma treated and sample 2 was plasma-treated and then sprayed with the dispersion.**

| Sample | Plasma parameters | | | | Results | | |
|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) | Oil rep. after 2000 cycles in Martindale |
| Reference | - | - | - | - | 142,4 | 6 | 4 |
| 1 | 1600 | 2.5 | 1 | 3 | 112,0 | 5 | 2 |
| 2 | 1600 | 2.5 | 1 | 3 | - | 6 | 3 |

The results from these trials showed that the contact angle was very high for the reference sample, lower for sample 1 and no contact angle could be measured for sample 2 since the drop would not adhere to the surface. The oil repellency show better values for the reference sample and sample 2 than sample 1, thus the plasma treatment deteriorated the hydrophobizing ability of the chemical. Hence, dispersion No.6 is not advisable to use with plasma treatment.

When comparing the oil repellency after the Martindale treatment the results indicate that the plasma treatment does not bind the fluoropolymers of the chemical harder to the surface of the fabric compared to the reference sample.

## 4.3.1 Scanning Electron Microscopy (SEM)

SEM was used to determine if the plasma caused any detrimental effect on the fabrics and if any apparent differences could be seen when comparing the fabric conventionally hydrophobized by FOV fabrics with the plasma treated ones. The following samples were evaluated with the apparatus:

- An untreated PET-textile
- Conventionally hydrophobized PET-textile
- Dispersion No.3 , Plasma treated with helium (Sample 1 table 19) 1600 W, 2.5, 1mm , 2 cycles – rinsed with distilled water.
- Dispersion No.3, Plasma treated with argon (Sample 2 table 19) 2000W, 4mm,2.5, 4 cycles

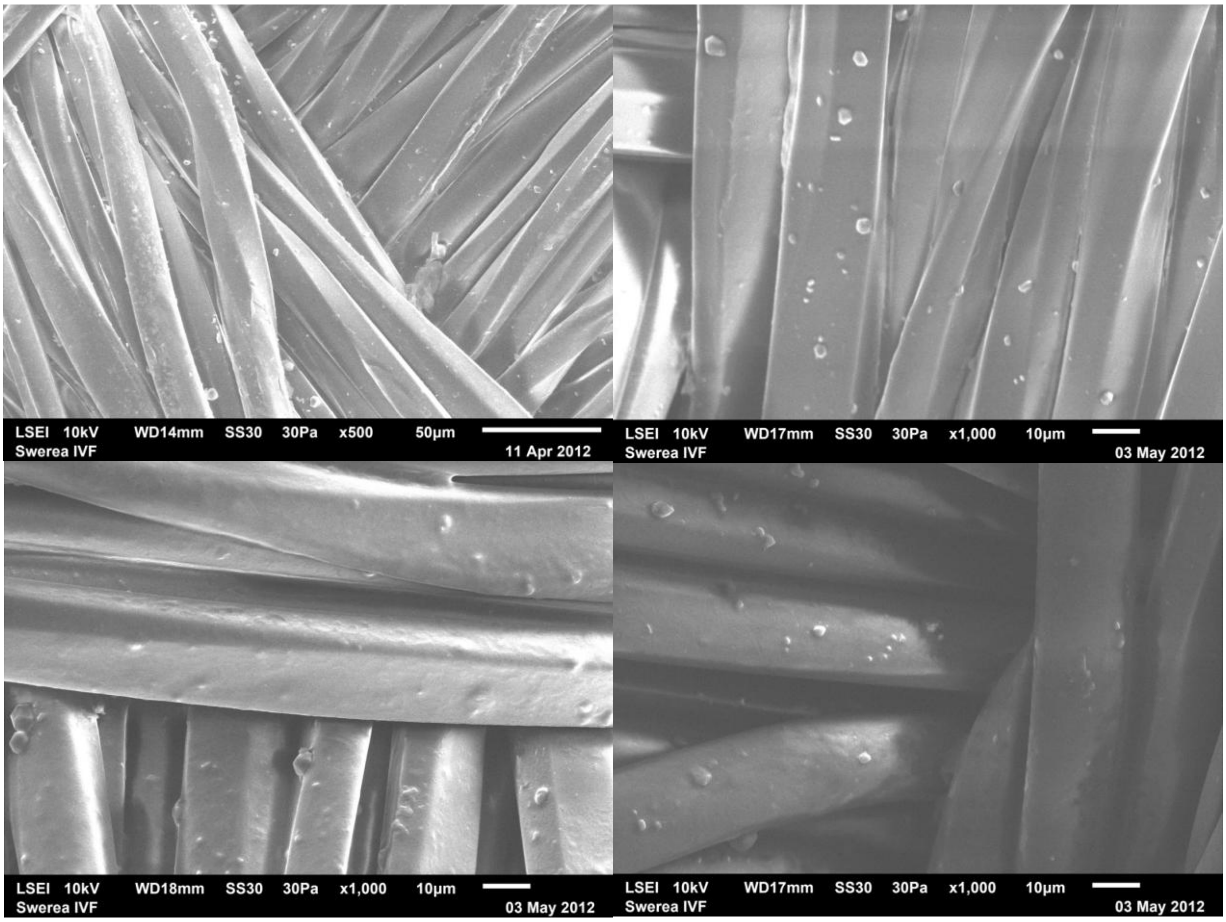


**Figure 16 SEM pictures of: Top left) Untreated PET-textile, Top right) Conventionally hydrophobzied PET-textile, Bottom left) PET-textile plasma treated with helium and Bottom right) PET-textile plasma treated with argon.**

As can be seen in Figure 16 the structure of the filament yarns of the PET-textile can be described as rounded with an angular shape. From the pictures taken of the different samples, no damaging effect could be seen on the plasma treated samples compared to the untreated one.

### 4.3.2 Electron Spectroscopy of Chemical Analysis (ESCA)

ESCA analysis was conducted to determine the elemental composition and the type of molecules that have adhered to the surface of the selected samples. The following samples were evaluated:

1. Untreated PET-fabric
2. Conventionally hydrophobized PET-textile
3. Chemical bath No.3 , Plasma treated with helium (Sample 1 table 19) 1600 W ,2.5, 1mm , 2 cycles – rinsed with distilled water.
4. A sample that had been soaked in chemical bath No.3 and then squeezed between two rollers but not plasma treated.

The result of the elemental analysis can be seen in Table 24 below.

**Table 24. Elemental analys – atomic composition at the surface of different samples.**

| Sample | C | N | O | F | Cl2p |
|---|---|---|---|---|---|
| 1 | 72.8 | - | 27.2 | - | |
| 2 | 46.2 | - | 7.5 | 45.5 | 0.81 |
| 3 | 54.7 | 1.0 | 11.4 | 32.5 | 0.29 |
| 4 | 60.9 | 2.2 | 11.2 | 24.8 | 1.03 |

The atomic concentrations of the surface of the untreated sample show that the PET-fabric consists of carbon and oxygen and no other compounds. While the three chemically treated samples all have a large percentage of fluorine atoms at the surface. The conventionally hydrophobized sample has the most fluorine content compared to the soaked and plasma treated sample. This might be due to the curing of the textile after the chemical has been applied. The heat makes the fluorinated carbon chains migrate to the surface from inside the filaments. This is a reasonable explanation since the soaked and the plasma treated samples all have been exposed to a higher concentration of the chemical than the conventionally hydrophobized one. ESCA is a surface-sensitive technique and provides information of molecular composition to a depth of approximately 5 nm.

The fluorine content is lower in the soaked sample compared to the plasma treated one. This might be due to stronger bonds between the fluorine and the substrate as a result of the plasma treatment. ESCA operates under low pressure meaning that any covalently attached molecules on the fibers will evaporate prior to measurement. Hence, these results are in favor of the suggestion that the plasma energy makes molecules bind covalently to the fiber surface.

Low amounts of chlorine can also be found in the chemically treated samples. AFR6 contains chlorinated monomers that give an improved film formation and orientation of the polymer.

There is also a small percentage of nitrogen found in both the soaked and plasma treated sample. The reason for this is that the AFR6 chemical consists of small amounts of quaternary ammonia compounds, according to the material safety data sheet. The absence of the nitrogen in the conventionally treated fabric is probably only coincidental and should not be related to the curing of the fabric.

*Peaks with related binding energies for* carbon

In order to determine what molecules that are present and to what extent, the binding energies and the area percentage of the ESCA results needs to be evaluated. The chemical shift of carbon is used to determine the functional groups at the surface. In Table 25 below the binding energies (Pos) and the area percentage is seen for the untreated PET-textile.

**Table 25. Three peaks from the C1 shift of a PET-textile sample.**

| Sample | Peak | Pos | %Area |
|---|---|---|---|
| 1 | 1 | 284.16 | 66.97 |
| | 2 | 285.77 | 21.55 |
| | 3 | 288.15 | 11.49 |

In the spectrum of the PET-fabric three carbon groups are observed. Knowing the structure of PET and checking literature data [27]for binding energies the first peak is determined as an aromatic carbon at 284.16 eV, the second peak is a C-O bonded carbon at a binding energy of 285.77 and the last peak is a O-C=O bonded carbon at 288.15 eV.

The peaks and binding energies of the chemically treated fabrics can be seen in Table 26. An assumption is made that the fluorocarbon forms a layer which is thinner than 5 nm, thus three of the peaks for each sample are related to the underlying PET-fabric and not to the hydrophobizing chemical.

**Table 26. Peaks and binding energies of the chemically treated samples.**

| Sample | Peak | Pos | %Area |
|---|---|---|---|
| 2 | 1 | 284.71 | 41.1 |
| | 2 | 286.15 | 12.1 |
| | 3 | 287.15 | 2.9 |
| | 4 | 288.64 | 8.5 |
| | 5 | 291.23 | 29.5 |
| | 6 | 293.49 | 5.9 |
| 3 | 1 | 284.34 | 40.9 |
| | 2 | 285.76 | 26.8 |
| | 3 | 287.02 | 2.94 |
| | 4 | 288.50 | 8.5 |
| | 5 | 291.06 | 17.1 |
| | 6 | 293.46 | 3.7 |
| 4 | 1 | 284.29 | 57.9 |
| | 2 | 285.79 | 21.6 |
| | 3 | 288.38 | 6.7 |
| | 4 | 291.08 | 11.5 |
| | 5 | 293.45 | 2.5 |

For the conventionally treated fabric the peaks 1, 2 and 4 are most likely to correspond with peak 1,2 and 3 from the untreated sample, given that the hydrophobizing chemical does not form a film that is thicker than 5 nm, which is the approximate depth of analysis in ESCA. The three other peaks are most likely functional groups containing fluorine in different forms. Peak number 3 might be $[-CHF-CH_2-]_n$. Peak 5 which is found in a large amount could be the functional group $C-F_2$ in the following forms $[-CF_2-CH_2-]_n$ or $[-CF_2-CF-]$. The last peak could be the functional group $C-F_3$ in different forms or $[-O-CF_2-]_n$. The plasma treated sample also shows six peaks with similar binding energies as for the conventionally treated fabric so it is fair to assume that they consist of the same functional groups [27].

For the sample that was only immersed in the dispersion, and not plasma treated, only five peaks are visible where peak 1-3 are likely to correspond to the same peaks (aromatic carbon at 284.29 eV, C-O bonded carbon at a binding energy of 285.79 and the last peak is a O-C=O bonded carbon at 288.38 eV in the untreated sample.

The two other peaks for this sample corresponds to the last two peaks of the plasma treated samples ( $[-CF_2-CH_2-]_n$ or $[-CF_2-CF-]$ and $[-O-CF_2-]_n$). The peak that is “missing” for the soaked sample might be due to that no hydrogen atoms has been replaced by fluorine atoms in the PET-structure, due to lack of energy needed for a substitution.

## Conclusion

From the results of the vacuum plasma treated samples it is obvious that it is possible to hydrophobize the textiles using $CF_4$ as the process gas alone or in combination with the chemicals AFR6 with or without EPF 2023. Argon gas on the other hand showed a tendency to remove the fluorocarbons by etching, when using it in combination with the AFR6 or AFR6/EPF 2023.

The best results for the earlier trials with the vacuum plasma was achieved for the samples that were pre-dried, sprayed with dispersion No 3 and cured for 1 min, 170°C before treated with the plasma. The results also show that the power was not a determining factor to achieve a hydrophobic surface, although it is obvious that the plasma treatment was necessary to achieve hydrophobicity when comparing with the various contact angles received for the cured reference samples. Most of the reference samples were not even presented in the graphs because of their hydrophilic properties but can be seen in the Appendix.

The trials with the vacuum plasma that were conducted at a later stage of the diploma work were immersed in dispersion No 3 and not sprayed. They showed, however, similar contact angles to the previously chemically- and plasma treated samples but also a good oil repellency.

The best results achieved when using the APP was seen when using dispersion No 3, giving high contact angles and great oil repellency. The APP samples showed higher contact angles and a greater oil repellency than the vacuum plasma treated samples. When comparing the APP results with the two conventionally treated fabrics, one hydrophobized by FOV fabrics and one immersed in dispersion number 3 at Swerea IVF, it is clear that the oil repellency is equal or better for the APP treated samples than for the references that were treated with the same chemicals but not plasma treated. What is also clearly seen after the abrasion testing is that the oil repellency is higher for the APP treated samples, which leads to the conclusion that the APP makes the fluorocarbons bind harder to the fabric than when heat is used, which is the case within the conventional hydrophobisation process.

It is however surprising to see the results of the water spray testing of samples for which the oil repellency showed great results. The fabric that was plasma treated was easily wetted when conducting this test and the reason for this has nothing to do with the plasma damaging the fabric in any way since the SEM pictures showed no such effects as well as studying the fabric with a light microscope.

To achieve hydrophobic properties on the fabric a concentrated dispersion of the chemical was needed. Trials that were conducted with diluted dispersions showed poor results (Appendix). Since the aim of the project was to try to develop a new processing method for the hydrophobization of textiles with a lesser use of chemicals the conclusion is that new chemicals needs to be tested since the AFR6 does not give satisfactory results in low concentrations in combination with the APP.

When comparing the results from a conventionally treated fabric, produced at Swerea IVF, with the APP treated sample immersed in dispersion No 3 the (sample 7 Table 18 for instance) oil repellency was about the same . However, the APP treated sample showed a better oil repellency after 2000 cycles in the Martindale apparatus but had a significant lower spray test grading (5 for the conventionally treated sample and 1 for the APP treated sample).

The samples that were sprayed with the Flexipel AM-95 showed great oil repellency without any plasma treatment or heat and showed great results even after the abrasion testing. Perhaps a good chemical is a better option than both the conventional method as well as any plasma treatment. It should be stated though that this product is approximately 4 times more expensive and was only diluted 1:10 to achieve those results. A dispersion in the industry, for the conventional method, usually only contains 2- 10% of the active hydrophobizing chemical.

## Future work

For further research different chemicals could be used, preferably chemicals that have been tailor-made to suit the plasma technology. Such chemicals would contain vinylic bonds and have lower molecular weight than the more or less polymeric compounds, evaluated within the scope of this project. In this thesis the majority of research was conducted on the AFR6 chemical which is tailor made for the conventional method of hydrophobizing textiles, using heat for curing. It is also important to reduce the use of hydrophobizing chemicals, to be able to call the plasma treatment a more environmentally friendly process.

Instead of liquid fluoro-containing chemicals, fluorinated gases would also be an option to achieve great results, as indicated by the vacuum plasma results in this project, perhaps with the combination of exposing the fabric to a dispersion of dendrimers.

There is also a spraying equipment connected to the APP apparatus that has not yet been tested. To spray the fabric simultaneously or directly after it comes out of the plasma zone might be promising, since the textile surface then contains a greater number of reactive sites, to which the hydrophobizing agent may adhere in a permanent way. Some of this reactivity disappears quickly after plasma treatment.

Finally, research on other fabrics might also be of interest, for instance cotton or wool.

# References

1. Teli, M.D, Shrish Kumar, G. V. N. (2007) Functional Textiles and Apparels. *Journal of the Textile Association,* pp. 21-30.

2. Shishoo, R. (2007) Introduction. *Plasma technologies for textiles*. Shishoo, R. Abington: Woodhead Publishing Limited

3. Garbassi F, Morra M, Occhiellol E. (1998) *Polymer surfaces,* Chichester: John Wiley & Sons

4. Jensen, A. A, Brunn Poulsen, P. (2008) Survey and environmental/health assessment of fluorinated substances in impregnated consumer products and impregnating agents. *Survey of Chemical Substances in Consumer Products*, No 99.

5. John, M. J, Anandjiwala, M. J. (2009) Surface modification and preparation techniques for textile materials. *Surface Modification of Textiles,* Wei, Q. Boca Raton: Woodhead Publishing Limited.

6. Jaffe, M. East, A. J. (2006) Polyester Fibers. *Handbook of Fiber Chemistry.* Third Edition. Lewin, M. Boca Raton: CRC Press.

7. Hatch, K.L. (1993) *Textile Science,* Minneapolis: West Publishing Company

8. Broadbent, A. (2001) *Basic Principles of Textile Coloration*, West Yorkshire: Dyers Company Publications Trust

9. Holmberg, K et al. (2004) *Surfactants and Polymers in Aqueous Solution,* Chichester: John Wiley & Sons Ltd

10. Sahin, B. (1996) Fluorochemicals in textile finishing. Reader's Service*,* vol. 3, no 5-576, pp. 26-30.

11. Environmental Protection Agency (2012) Perfluorooctanoic Acid (PFOA) and Fluorinated Telomers. *http://www.epa.gov/oppt/pfoa/* (6 June 2012).12. The Swedish Government (2011) Reglering av kemikalier på EU-nivå. *http://www.regeringen.se/sb/d/6043* *(*6 June 2012).

13. UK Ministry of Defense (2010) Hazardous substances and restricted materials. *http://www.mod.uk/NR/rdonlyres/AB301FAC-6D9C-4BC2-A712-C6654933DD52/0/JSP_418_Leaflet05.pdf* (6 June 2012).

14. Bluesign (2010) Bluesign Criteria for Textile Manufacturers *http://www.bluesign.com/index.php?id=151* *(*6 June 2012).

15. Oeko-Tex (2012) Limit Values and Fastness. *http://www.oeko-tex.com/OekoTex100_PUBLIC/content1.asp?area=hauptmenue&site=grenzwerte&cls=21* (6 June 2012)

16. Buyle, G. et al. (2010) Tuning the Surface Properties of Textile Materials. *Plasma Technology for Hyperfunctional Surfaces,* Rausher, H. et al. Weinheim: Wiley-VCH Verlag GmbH

17. Tendero, C. et al. (2006) Atmospheric pressure plasmas: A Review. *Spectrochimica Acta Part B*, no 61, pp. 2-30.

18. Boulos, M. I. (1991) Thermal Plasma Processing. *IEEE Transactions on Plasma Science,* vol 19, no 6.

19. Lippens, P. (2007) Low-pressure cold plasma proceesing technology. *Plasma technologies for textiles*. Shishoo, R. Abington: Woodhead Publishing Limited

20. Laroussi, M. (2002) Cold Plasma. In *AccessScience.* http://www.accessscience.com (6 June 2012)

21. Herbert, T. (2007)Atmospheric-pressure cold plasma processing technology. *Plasma technologies for textiles*. Shishoo, R. Abington: Woodhead Publishing Limited

22. Moore, R. (2008) Plasma surface functionalization of textiles. *Institute of Nanotechnology* *http://www.acteco.org/Acteco/public/results/MOORE_IoN_March08.pdf* (7June 2012)

23. Nazirul Islam, Md. (2004) *Fundamental investigations on the barrier effect of polyester micro fiber fabrics towards particle-loaded liquids induced by surface hydrophobization.* Der Technischen Universität Dresden.

24. Morent R et al. (2007) Surface modification of non-woven textiles using a dielectric barrier discharge operating in air helium and argon at medium pressure*, Textile Research Journal,* Vol 77, No7, pp 471-488

25. Morent, R et al. (2008) Non-thermal plasma treatment of textiles. *Surface & CoatingTechnology 202,* pp. 3427-3449.

26. David, A. et al. (2010) Surface Analysis for Plasma Treatment Characterization. *Plasma Technology for Hyperfunctional Surfaces,* Rausher, H. et al. Weinheim: Wiley-VCH Verlag GmbH

27. Moulder, J.F. et al. (1992), *Handbook of X-ray Photoelectron Spectroscopy*, Phys. Electr. Division, Perkin Elmer Corporation.

# Appendix A

In this Appendix all the raw data is presented for all vacuum- and atmospheric pressure plasma samples. All samples have been treated with either $CF_4$ or argon as the process gas.

## Vacuum plasma raw data

**Table 27. Untreated polyester textile with no purge ($CF_4$)**

| Sample | Time [s] | Cycles | Power [W] | Contact angle (Left, Right angle) [°] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | | 2 | | 3 | | Average value | Standard deviation |
| 1 | 10 | - | 300 | 118,3 | 115,8 | 121,8 | 120,4 | 93,7 | 95,7 | 111 | 12,76476 |
| 2 | 10 | 5 | 300 | 140,1 | 138,2 | 134,9 | 134,3 | 134,8 | 133,3 | 135,9 | 2,625008 |
| 3 | 30 | - | 300 | 110,5 | 110,4 | 115,4 | 114,6 | 118,3 | 118,5 | 114,6 | 3,577383 |
| 4 | 30 | 5 | 300 | 131,3 | 130,9 | 135,9 | 135,4 | 128,7 | 128,4 | 131,8 | 3,224696 |
| 5 | 10 | - | 650 | 125,5 | 125,4 | 127,2 | 127,1 | 131,7 | 132,2 | 128,2 | 3,019547 |
| 6 | 10 | 5 | 650 | 135 | 136,2 | 133,1 | 132,9 | 125,2 | 125,2 | 131,3 | 4,856199 |
| 7 | 30 | - | 650 | 135,6 | 135,4 | 135,2 | 135,8 | 126 | 126 | 132,3 | 4,909854 |
| 8 | 30 | 5 | 590 | 126,5 | 126 | 128,4 | 128,7 | 122,8 | 122,8 | 125,9 | 2,595124 |

**Table 28. Water soaked textiles ($CF_4$)**

| Sample | Time [s] | Cycles | Power [W] | Contact angle (Left, Right angle) [°] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | | 2 | | 3 | | Average value | Standard deviation |
| 1 | 10 | - | 300 | 27,2 | 29,1 | 0 | 0 | 83,1 | 83,9 | 37 | 38,0026 |
| 2 | 10 | 5 | 300 | 131,5 | 132,3 | 124,5 | 124,6 | 121,6 | 120,1 | 125,8 | 5,059512 |
| 3 | 30 | - | 300 | 129,3 | 129,5 | 123,2 | 122,6 | 114,1 | 113,9 | 122,1 | 6,918092 |
| 4 | 30 | 5 | 300 | 123,6 | 123,9 | 124,3 | 123,3 | 132,9 | 132,2 | 126,7 | 4,548846 |
| 5 | 10 | - | 600 | 113,5 | 113,6 | 124,4 | 124,2 | 120,1 | 120 | 119,3 | 4,843139 |
| 6 | 10 | 5 | 600 | 125,7 | 124,5 | 136 | 135,2 | 124,8 | 123,6 | 128,3 | 5,699825 |
| 7 | 30 | - | 600 | 120,4 | 121,2 | 135,5 | 135,3 | 131,5 | 131,9 | 129,3 | 6,794998 |
| 8 | 30 | 5 | 600 | 129,3 | 128,8 | 119,6 | 119,7 | 134,2 | 134 | 127,6 | 6,561402 |

**Table 29. Purged samples ($CF_4$)**

| Sample | Time [s] | Cycles | Power [W] | Contact angle (Left, Right angle) [°] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | | 2 | | 3 | | Average value | Standard deviation |
| 1 | 10 | - | 300 | 124,6 | 127 | 0 | 0 | 0 | 0 | 41,9 | 64,96727 |
| 2 | 10 | 5 | 300 | 120,5 | 120,2 | 136,5 | 136,3 | 131,4 | 131 | 129,3 | 7,326504 |
| 3 | 30 | - | 300 | 132,4 | 132,9 | 130,6 | 130,3 | 133,7 | 132,8 | 132,1 | 1,361494 |
| 4 | 30 | 5 | 300 | 131,2 | 131,7 | 126,7 | 126 | 122,4 | 118,4 | 126,1 | 5,11299 |
| 5 | 10 | - | 600 | 121,6 | 119,3 | 116,1 | 116 | 128,4 | 127,8 | 121,5 | 5,505512 |
| 6 | 10 | 5 | 600 | 130 | 130,4 | 131,8 | 132 | 131,3 | 132,5 | 131,3 | 0,966782 |
| 7 | 30 | - | 600 | 125,2 | 124,9 | 131,6 | 131,3 | 134,9 | 134,2 | 130,35 | 4,340852 |
| 8 | 30 | 5 | 600 | 134,8 | 134,4 | 127,3 | 126,8 | 130,5 | 130,9 | 130,8 | 3,385508 |

**Table 30. Pre-dried in oven for 1min at 100°C ($CF_4$)**

| Sample | Time [s] | Cycles | Power [W] | Contact angle (Left, Right angle) [°] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | | 2 | | 3 | | Average value | Standard deviation |
| 1 | 10 | - | 300 | 97,5 | 101,5 | 0 | 0 | 0 | 0 | 33,2 | 51,39715 |
| 2 | 10 | 5 | 300 | 124 | 123,8 | 123,8 | 124 | 126,2 | 126,2 | 124,7 | 1,191078 |
| 3 | 30 | - | 300 | 108,8 | 107,5 | 80,6 | 83,4 | 0 | 0 | 63,4 | 50,47956 |
| 4 | 30 | 5 | 300 | 117,7 | 117,9 | 128,8 | 128,8 | 127,4 | 127,6 | 124,7 | 5,376988 |
| 5 | 10 | - | 600 | 120 | 120,2 | 120,7 | 120,4 | 0 | 0 | 80,2 | 62,13599 |
| 6 | 10 | 5 | 600 | 121 | 120,5 | 119,9 | 119,2 | 114 | 113,3 | 118 | 3,41726 |
| 7 | 30 | - | 600 | 124,6 | 125,4 | 123,2 | 122,7 | 122 | 121,1 | 123,2 | 1,605823 |
| 8 | 30 | 5 | 600 | 120,2 | 119,7 | 123,4 | 120,4 | 126,6 | 127,1 | 122,9 | 3,327461 |

**Table 31. Pre-dried for 1 min at 100 °C, AFR6 sprayed and cured for 1 min at 170 °C ($CF_4$)**

| Sample | Time [s] | Cycles | Power [W] | Contact angle (Left, Right angle) [°] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | | 2 | | 3 | | Average value | Standard deviation |
| Reference | | | | 121,6 | 121,6 | 132,1 | 131,7 | 138,4 | 138,6 | 130,7 | 7,619361 |
| 1 | 10 | - | 300 | 135,6 | 135,4 | 123,7 | 124 | 130,4 | 129,8 | 129,82 | 5,219355 |
| 2 | 10 | 5 | 300 | 132,2 | 132,3 | 127,3 | 127,5 | 138,7 | 138,4 | 132,7 | 5,001866 |
| 3 | 30 | - | 300 | 131,9 | 131,7 | 132,1 | 132,3 | 134,3 | 133,9 | 132,7 | 1,109955 |
| 4 | 30 | 5 | 300 | 122,1 | 121,9 | 128,2 | 127,8 | 125,6 | 125,6 | 125,2 | 2,704811 |
| 5 | 10 | - | 600 | 136,2 | 136,9 | 136,4 | 136,4 | 143,8 | 143,2 | 138,8 | 3,640009 |
| 6 | 10 | 5 | 600 | 127,3 | 126,7 | 127,4 | 126,3 | 129 | 129,6 | 127,7 | 1,304479 |
| 7 | 30 | - | 600 | 133,8 | 132,2 | 134,5 | 135 | 129,4 | 129,2 | 132,4 | 2,545388 |
| 8 | 30 | 5 | 600 | 118,5 | | 109,8 | | 114,6 | | 114,3 | 4,357752 |

Sample 8 was conducted on a different apparatus at Chalmers University of Technology which only gave one value of the contact angle instead of a left and right angle.

**Table 32. Pre-dried for 1 min at 100 °C, AFR6 sprayed and plasma treated with argon gas.**

| Sample | Time [s] | Cycles | Power [W] | Contact angle [°] | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 | Average value | Standard deviation |
| Reference | | | | 0 | 0 | 68,5 | 22,8 | 39,54849 |
| 1 | 10 | - | 300 | 0 | 0 | 0 | 0 | 0 |
| 2 | 10 | 5 | 300 | 0 | 0 | 0 | 0 | 0 |
| 3 | 30 | - | 300 | 0 | 0 | 0 | 0 | 0 |
| 4 | 30 | 5 | 300 | 0 | 0 | 0 | 0 | 0 |
| 5 | 10 | - | 600 | 0 | 0 | 0 | 0 | 0 |
| 6 | 10 | 5 | 600 | 0 | 0 | 0 | 0 | 0 |
| 7 | 30 | - | 600 | 0 | 0 | 0 | 0 | 0 |
| 8 | 30 | 5 | 600 | 101,5 | 110,3 | 0 | 70,6 | 61,29951 |

**Table 33. Pre-dried for 1 min at 100 °C, AFR6 sprayed and cured for 5 min at 170 °C before being plasma treated. ($CF_4$)**

| Sample | Time [s] | Cycles | Power [W] | Contact angle [°] | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 | Average value | Standard deviation |
| Reference | | | | 43,5 | 49 | 24,3 | 38,9 | 12,96778 |
| 1 | 10 | - | 300 | 108,6 | 110,9 | 112,8 | 110,8 | 2,103172 |
| 2 | 10 | 5 | 300 | 117,1 | 112,7 | 119,7 | 116,5 | 3,538361 |
| 3 | 30 | - | 300 | 116,6 | 124,3 | 117,9 | 119,6 | 4,121893 |
| 4 | 30 | 5 | 300 | 118,3 | 122,4 | 120,6 | 120,4 | 2,055075 |
| 5 | 10 | - | 600 | 119,1 | 117,5 | 103,6 | 113,4 | 8,52467 |
| 6 | 10 | 5 | 600 | 130,2 | 119,6 | 117,5 | 122,4 | 6,807594 |
| 7 | 30 | - | 600 | 127,4 | 122,6 | 122,5 | 124,2 | 2,800595 |
| 8 | 30 | 5 | 600 | 118,6 | 121,1 | 116,2 | 118,6 | 2,45017 |

**Table 34. Pre-dried for 1 min at 100 °C, AFR6 sprayed. ($CF_4$)**

| Sample | Time [s] | Cycles | Power [W] | Contact angle [°] | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 | Average value | Standard deviation |
| Reference | | | | 0 | 0 | 0 | 0 | 0 |
| 1 | 10 | - | 300 | 86 | 0 | 35,5 | 40,5 | 43,21747 |
| 2 | 10 | 5 | 300 | 106,4 | 96,4 | 111,2 | 104,7 | 7,550717 |
| 3 | 30 | - | 300 | 111,1 | 118,8 | 121,5 | 117,1 | 5,396604 |
| 4 | 30 | 5 | 300 | 119,6 | 128,2 | 120 | 122,6 | 4,853864 |
| 5 | 10 | - | 600 | 116,8 | 115,5 | 117 | 116,4 | 0,814453 |
| 6 | 10 | 5 | 600 | 117,1 | 114,6 | 119,2 | 117 | 2,302897 |
| 7 | 30 | - | 600 | 121,1 | 121,6 | 117,2 | 120 | 2,409011 |
| 8 | 30 | 5 | 600 | 117,6 | 114,5 | 119,5 | 117,2 | 2,523886 |

**Table 35. Pre-dried for 1 min at 100 °C, AFR6 sprayed and cured for 1 min at 170 °C before being plasma treated with argon gas.**

| Sample | Time [s] | Cycles | Power [W] | Contact angle [°] | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 | Average value | Standard deviation |
| Reference | | | | 130,8 | 133,3 | 133,6 | 132,6 | |
| 1 | 10 | - | 300 | 118 | 98,3 | 126 | 114,1 | 10 |
| 2 | 10 | 5 | 300 | 0 | 0 | 0 | 0 | 10 |
| 3 | 30 | - | 300 | 0 | 0 | 0 | 0 | 30 |
| 4 | 30 | 5 | 300 | 30,5 | 20 | 19 | 23,2 | 30 |
| 5 | 10 | - | 600 | 85 | 0 | 0 | 28,3 | 10 |
| 6 | 10 | 5 | 600 | 114,8 | 112,9 | 113 | 113,6 | 10 |
| 7 | 30 | - | 600 | 0 | 102,1 | 0 | 34 | 30 |
| 8 | 30 | 5 | 600 | 120 | 120,9 | 120 | 120,3 | 30 |

**Table 36. Pre-dried for 1 min at 100 °C, AFR6/EPF 2023 sprayed and cured for 1 min at 170 °C before being plasma treated with argon gas.**

| Sample | Time [s] | Cycles | Power [W] | Contact angle [°] | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 | Average value | Standard deviation |
| Reference | | | | 49,1 | 31,8 | 104,9 | 61,9 | 38,2024 |
| 1 | 10 | - | 300 | 0 | 0 | 0 | 0 | 0 |
| 2 | 10 | 5 | 300 | 0 | 0 | 0 | 0 | 0 |
| 3 | 30 | - | 300 | 0 | 0 | 0 | 0 | 0 |
| 4 | 30 | 5 | 300 | 0 | 0 | 0 | 0 | 0 |
| 5 | 10 | - | 600 | 0 | 0 | 0 | 0 | 0 |
| 6 | 10 | 5 | 600 | 0 | 0 | 0 | 0 | 0 |
| 7 | 30 | - | 600 | 0 | 0 | 0 | 0 | 0 |
| 8 | 30 | 5 | 600 | 0 | 0 | 0 | 0 | 0 |

**Table 37. Pre-dried for 1 min at 100 °C, AFR6/EPF 2023 sprayed and cured for 1 min at 170 °C before being plasma treated with $CF_4$**

| Sample | Time [s] | Cycles | Power [W] | Contact angle [°] | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 | Average value | Standard deviation |
| Reference | | | | 84,5 | 104,2 | 111,3 | 100,6 | 13,88488 |
| 1 | 10 | - | 300 | 102,9 | 113,5 | 117,6 | 111,3 | 7,585732 |
| 2 | 10 | 5 | 300 | 109,1 | 113,4 | 110,8 | 111,1 | 2,165641 |
| 3 | 30 | - | 300 | 115,3 | 119,7 | 126,3 | 120,4 | 5,536545 |
| 4 | 30 | 5 | 300 | 117,1 | 115,5 | 119,4 | 117,3 | 1,960442 |
| 5 | 10 | - | 600 | 125,5 | 117,4 | 122,3 | 121,7 | 4,079624 |
| 6 | 10 | 5 | 600 | 113,1 | 119,4 | 121,7 | 118,1 | 4,45234 |
| 7 | 30 | - | 600 | 119,3 | 111,6 | 115,3 | 115,4 | 3,850974 |
| 8 | 30 | 5 | 600 | 118,8 | 119,3 | 114,5 | 117,5 | 2,638813 |

# APP raw data

All samples were plasma treated with helium as the process gas if nothing else is mentioned.

## Dispersion No. 1

### *Dry samples*

The dry samples were immersed in the dispersion, calendered, left to dry over night at R.T. before being plasma treated.

**Table 38. Plasma parameters for dry samples.**

| Sample | Plasma parameters | | | |
|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles |
| 1 | 400 | 2 | 3 | 1 |
| 2 | 400 | 2 | 4 | 1 |
| 3 | 400 | 2 | 5 | 1 |
| 4 | 600 | 2 | 3 | 1 |
| 5 | 600 | 2 | 4 | 1 |
| 6 | 600 | 2 | 5 | 1 |
| 7 | 800 | 2 | 3 | 1 |
| 8 | 800 | 2 | 4 | 1 |
| 9 | 800 | 2 | 5 | 1 |

**Table 39. Contact angles for dry samples.**

| Sample | Contact angle (Left, Right angle)[°] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | | 2 | | 3 | | Average value | Standard deviation |
| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 8 | 111 | 110,6 | 102 | 103,7 | 96,4 | 97,1 | 103,466667 | 6,32950762 |
| 9 | 118 | 118,2 | 108,2 | 108,5 | 98,8 | 99,7 | 108,566667 | 8,43721913 |

### *Semi dry samples*

The semi dry samples were immersed in the dispersion, calendered and left to dry for 2h at R.T before being plasma treated.

**Table 40. Plasma parameters for semi dry samples.**

| Sample | Parametrar | | | |
|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes[mm] | No. of cycles |
| 1 | 400 | 2 | 3 | 4 |
| 2 | 400 | 2 | 4 | 4 |
| 3 | 400 | 2 | 5 | 4 |
| 4 | 600 | 2 | 3 | 4 |
| 5 | 600 | 2 | 4 | 4 |
| 6 | 600 | 2 | 5 | 4 |
| 7 | 800 | 2 | 3 | 4 |
| 8 | 800 | 2 | 4 | 4 |
| 9 | 800 | 2 | 5 | 4 |

**Table 41. Contact angles for semi dry samples.**

| Sample | Contact angle (Left, Right angle)[°] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | | 2 | | 3 | | Average value | Standard deviation |
| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 9 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |

**Table 42. Plasma parameters for semi dry samples with increased power.**

| Sample | Plasma parameters | | | |
|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles |
| 1 | 1200 | 2.5 | 3 | 4 |
| 2 | 1200 | 2.5 | 4 | 4 |
| 3 | 1200 | 2.5 | 5 | 4 |
| 4 | 1600 | 2.5 | 3 | 4 |
| 5 | 1600 | 2.5 | 4 | 4 |
| 6 | 1600 | 2.5 | 5 | 4 |
| 7 | 2000 | 2.5 | 3 | 4 |
| 8 | 2000 | 2.5 | 4 | 4 |

**Table 43. Contact angles for semi dry samples with increased power.**

| Sample | Contact angle (Left, Right angle)[°] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | | 2 | | 3 | | Average value | Standard deviation |
| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |

### *Samples that were plasma treated before being immersed in the dispersion.*

**Table 44. Plasma parameters for samples that were first plasma treated and then immersed in the dispersion.**

| Sample | Plasma parameters | | | |
|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles |
| 1 | 1200 | 2.5 | 3 | 4 |
| 2 | 1200 | 2.5 | 4 | 4 |
| 3 | 1200 | 2.5 | 5 | 4 |
| 4 | 1600 | 2.5 | 3 | 4 |
| 5 | 1600 | 2.5 | 4 | 4 |
| 6 | 1600 | 2.5 | 5 | 4 |
| 7 | 2000 | 2.5 | 3 | 4 |
| 8 | 2000 | 2.5 | 4 | 4 |
| 9 | 2000 | 2.5 | 5 | 4 |

**Table 45. Contact angles for samples that were first plasma treated and then immersed in the dispersion.**

| Sample | Contact angle (Left, Right angle)[°] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | | 2 | | 3 | | Average value | Standard deviation |
| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 9 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |

## Dispersion No. 2

### *Semi dry samples*

The semi dry samples were immersed in the dispersion, calendered and left to dry in R.T for 2 h before being plasma treated.

**Table 46. Plasma parameters for semi dry samples.**

| Sample | Parametrar | | | |
|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes[mm] | No. of cycles |
| 1 | 1200 | 2.5 | 3 | 4 |
| 2 | 1200 | 2.5 | 4 | 4 |
| 3 | 1200 | 2.5 | 5 | 4 |
| 4 | 1600 | 2.5 | 3 | 4 |
| 5 | 1600 | 2.5 | 4 | 4 |
| 6 | 1600 | 2.5 | 5 | 4 |
| 7 | 2000 | 2.5 | 3 | 4 |
| 8 | 2000 | 2.5 | 4 | 4 |
| 9 | 2000 | 2.5 | 5 | 4 |

**Table 47. Contact angles for semi dry samples**

| Sample | Contact angle (Left, Right angle)[°] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | | 2 | | 3 | | Average value | Standard deviation |
| 1 | 92,2 | 91,3 | 87,1 | 85,1 | 76,9 | 74,2 | 84,4666667 | 7,436307327 |
| 2 | 104,9 | 99,9 | 93,1 | 94,1 | 65,9 | 71,5 | 88,2333333 | 15,81627853 |
| 3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | - |
| 9 | 108,3 | 106,8 | 86,5 | 85,8 | 92,9 | 98,5 | 96,4666667 | 9,764971411 |

## Dispersion No. 3

### *Wet samples*

Wet samples were immersed in the dispersion, calendered and plasma treated while still being wet.

**Table 48. Plasma parameters, contact angles and oil repellency for wet samples.**

| Sample | Plasma parameters | | | | Results | |
|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) |
| 1 | 1200 | 2.5 | 3 | 4 | 98,1 | 6 |
| 2 | 1200 | 2.5 | 4 | 4 | 123,4 | 5 |
| 3 | 1200 | 2.5 | 5 | 4 | 129,3 | 5 |
| 4 | 1600 | 2.5 | 3 | 4 | 137,6 | 7/8 |
| 5 | 1600 | 2.5 | 4 | 4 | 103,0 | 7/8 |
| 6 | 1600 | 2.5 | 5 | 4 | 135,8 | 7/8 |
| 7 | 2000 | 2.5 | 3 | 4 | 136,1 | 7/8 |
| 8 | 2000 | 2.5 | 4 | 4 | 141,5 | 7/8 |

**Table 49. Plasma parameters, contact angles and oil repellency for wet samples with a lower speed of the frame and a lower distance between the electrodes. Also a reference sample that was treated the same but with no plasma treatment.**

| Sample | Plasma parameters | | | | Results | |
|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) |
| Reference | - | - | - | - | 67,0 | 2 |
| 1 | 1200 | 1.9 | 2 | 4 | 117,3 | 6 |
| 2 | 1200 | 1.9 | 3 | 4 | 133,1 | 6 |
| 3 | 1200 | 1.9 | 4 | 4 | 124,1 | 6 |
| 4 | 1600 | 1.9 | 2 | 4 | 111,3 | 6 |
| 5 | 1600 | 1.9 | 3 | 4 | 132,6 | 7 |
| 6 | 1600 | 1.9 | 4 | 4 | 131,2 | 7/8 |
| 7 | 2000 | 1.9 | 2 | 4 | 112,1 | 5 |
| 8 | 2000 | 1.9 | 3 | 4 | 104,7 | 7/8 |
| 9 | 2000 | 1.9 | 4 | 4 | 130,3 | 6 |

### *Dry samples*

The dry samples were immersed in the dispersion, calendered, left to dry over night at R.T. before being plasma treated.

**Table 50. Plasma parameters, contact angles and oil repellency for dry samples.**

| Sample | Plasma parameters | | | | Results | |
|---|---|---|---|---|---|---|
| | Power [W] | Average Contact Angle [°] | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) |
| 1 | 1200 | 2.5 | 3 | 4 | 133,7 | 6 |
| 2 | 1200 | 2.5 | 4 | 4 | 135,5 | 6/7 |
| 3 | 1200 | 2.5 | 5 | 4 | 137,9 | 6/7 |
| 4 | 1600 | 2.5 | 3 | 4 | 134,1 | 7/8 |
| 5 | 1600 | 2.5 | 4 | 4 | 134,1 | 6/7 |
| 6 | 1600 | 2.5 | 5 | 4 | 135,9 | 6/7 |
| 7 | 2000 | 2.5 | 3 | 4 | 132,1 | 7 |
| 8 | 2000 | 2.5 | 4 | 4 | 138,3 | 7 |
| 9 | 2000 | 2.5 | 5 | 4 | 129,4 | 6 |

**Table 51. Plasma parameters, contact angles and oil repellency of dry samples that were plasma treated with a lower speed of the frame and a lower distance between the electrodes.**

| Sample | Plasma parameters | | | | Results | |
|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electordes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) |
| 1 | 1200 | 1.9 | 2 | 4 | 135,8 | 7 |
| 2 | 1200 | 1.9 | 3 | 4 | 142,8 | 7/8 |
| 3 | 1200 | 1.9 | 4 | 4 | 143,4 | 7/8 |
| 4 | 1600 | 1.9 | 2 | 4 | 125,0 | 7/8 |
| 5 | 1600 | 1.9 | 3 | 4 | 133,7 | 7/8 |
| 6 | 1600 | 1.9 | 4 | 4 | 138,3 | 7/8 |
| 7 | 2000 | 1.9 | 2 | 4 | 131,3 | 7 |
| 8 | 2000 | 1.9 | 3 | 4 | 131,2 | 7/8 |

**Table 52. Plasma parameters, contact angles and oil repellency before and after 5000 cycles against wool fabric at 12 kPa.**

| Sample | Plasma parameters | | | | Resultat | | |
|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) | Oil rep. after 5000 cycles in Martindale |
| 1 | 1200 | 1.9 | 4 | 4 | 135,3 | 7 | 1 |
| 2 | 1600 | 1.9 | 2 | 4 | 138,1 | 7 | 1 |

.

**Table 53. Plasma parameters, contact angles, oil repellency and spray tested dry samples that had been rinsed with distilled water after plasma treatment.**

| Sample | Plasma parameters | | | | Results | | |
|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) | Spray test grading |
| 1 | 1200 | 1.9 | 4 | 4 | 135,7 | 6 | 1 |
| 2 | 1600 | 1.9 | 2 | 4 | 138,9 | 6/7 | 1 |
| 3 | 2000 | 2.5 | 3 | 4 | 134,7 | 7/8 | 1 |

**Table 54. Plasma parameters, contact angles, oil repellency before and after 2000 cycles in Martindale against wool fabric at 12 kPa for a dry fabric. The fabric was also spray tested after being plasma treated. The samples were rinsed with distilled water after being plasma treated.**

| Sample | Plasma parameters | | | | Results | | | |
|---|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) | Oil rep. after 2000 cycles in Martindale | Spray test grading |
| 1 | 3000 | 2.5 | 1 | 0 | 132,7 | 6 | - | 1 |
| 2 | 3000 | 2.5 | 1 | 4 | 131,0 | 6 | 3/4 | 1 |

**Table 55. Plasma parameters, contact angles, oil repellency before and after 2000 cycles in Martindale against wool fabric at 12 kPa for a dry fabric. The fabric was also spray tested after being plasma treated. The samples were rinsed with distilled water after being plasma treated.**

| Sample | Plasma parameters | | | | Results | | | |
|---|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) | Oil rep. after 2000 cycles in Martindale | Spray test grading |
| 1 | 1200 | 2.5 | 1 | 0 | 137,1 | 7/8 | 4 | 1 |
| 2 | 1200 | 2.5 | 1 | 2 | 138,8 | 7 | 4 | 1 |
| 3 | 1200 | 2.5 | 1 | 3 | 137,9 | 7 | 3/4 | 1 |
| 4 | 1600 | 2.5 | 1 | 0 | 138,0 | 7/8 | 3/4 | 1 |
| 5 | 1600 | 2.5 | 1 | 2 | 139,7 | 7/8 | 4 | 1 |
| 6 | 1600 | 2.5 | 1 | 3 | 140,4 | 6/7 | 4 | 1 |
| 7 | 2000 | 2.5 | 1 | 0 | 139,3 | 7/8 | 4 | 1 |
| 8 | 2000 | 2.5 | 1 | 2 | 135,2 | 7 | 4 | 1 |
| 9 | 2000 | 2.5 | 1 | 3 | 138,7 | 6/7 | 4 | 1 |

**Table 56. Plasma parameters, contact angles and oil repellency for a dry sample. The fabric was also spray tested after being plasma treated. A reference sample that was prepared in the same way but not plasma treated was also evaluated.**

| Sample | Plasma parameters | | | | | Results | |
|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Pickup [%] | Oil repellency (Highest liquid passed) | Spray test grading |
| Reference | - | - | - | - | 54,5 | 3 | 1 |
| 1 | 1600 | 2.5 | 1 | 3 | 53,3 | 5 | 1 |
| 2 | 1600 | 2.5 | 1 | 4 | 53,9 | 5 | 1 |

**Table 57. Plasma parameters and oil repellency for a dry sample. Sample 1-4 was treated with helium and sample 5-8 was treated with argon.**

| Sample | Plasma parameters | | | | | Results |
|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Pickup [%] | Oil repellency (Highest liquid passed) |
| 1 | 1600 | 2.5 | 1 | 4 | 45,7 | 5 |
| 2 | 1600 | 2.5 | 2 | 4 | 44,6 | 6 |
| 3 | 2000 | 2.5 | 1 | 4 | 45,9 | 5 |
| 4 | 2000 | 2.5 | 3 | 4 | 45,9 | 7 |
| 5 | 1600 | 2.5 | 1 | 4 | 48,2 | 6/7 |
| 6 | 1600 | 2.5 | 2 | 4 | 47,0 | 8 |
| 7 | 1600 | 2.5 | 3 | 4 | 46,4 | 6/7 |
| 8 | 1600 | 2.5 | 4 | 4 | 46,5 | 6 |

**Table 58. Plasma parameters, oil repellency before and after 2000/5000 cycles in Martindale against wool fabric at 12 kPA for dry samples plasma treated with argon.**

| Sample | Plasma parameters | | | | | Results | | |
|---|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Pickup [%] | Oil repellency (Highest liquid passed) | Oil rep. after 2000 cycles in Martindale | Oil rep. after 5000 cycles in Martindale |
| 1 | 1600 | 2.5 | 1 | 4 | 45,0 | 6 | 3 | 1 |
| 2 | 1600 | 2.5 | 2 | 4 | 45,6 | 7 | 3 | 1 |
| 3 | 1600 | 2.5 | 3 | 4 | 45,4 | 6 | 2 | 2 |
| 4 | 1600 | 2.5 | 4 | 4 | 46,5 | 6/7 | 2 | 2 |
| 5 | 2000 | 2.5 | 1 | 4 | 46,9 | 6 | 3 | 1 |
| 6 | 2000 | 2.5 | 2 | 4 | 45,5 | 7 | 3 | 1 |
| 7 | 2000 | 2.5 | 3 | 4 | 46,9 | 7 | 3/4 | 2 |
| 8 | 2000 | 2.5 | 4 | 4 | 46,0 | 7/8 | 3/4 | 3 |

*Samples that were plasma treated before being immersed in the dispersion.*

**Table 59. Plasma parameters, contact angles and oil repellency for samples that were plasma treated before being immersed in the dispersion.**

| Sample | Plasma parameters | | | | Results | |
|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) |
| 1 | 1200 | 1.9 | 2 | 4 | 119,8 | 3/4 |
| 2 | 1200 | 1.9 | 3 | 4 | 103,3 | 3/4 |
| 3 | 1200 | 1.9 | 4 | 4 | 113,5 | 3/4 |
| 4 | 1200 | 2.5 | 3 | 4 | 109,1 | 2 |
| 5 | 1200 | 2.5 | 4 | 4 | 113,5 | 3 |
| 6 | 1200 | 2.5 | 5 | 4 | 118,1 | 3 |
| 7 | 1600 | 1.9 | 2 | 4 | 109,9 | 3/4 |
| 8 | 1600 | 1.9 | 3 | 4 | 110,6 | 3/4 |
| 9 | 1600 | 1.9 | 4 | 4 | 118,5 | 3 |
| 10 | 1600 | 2.5 | 3 | 4 | 102,5 | 3 |
| 11 | 1600 | 2.5 | 4 | 4 | 116,4 | 3/4 |
| 12 | 1600 | 2.5 | 5 | 4 | 109,2 | 3 |
| 13 | 2000 | 1.9 | 2 | 4 | 131,1 | 3/4 |
| 14 | 2000 | 1.9 | 3 | 4 | 115,1 | 3/4 |
| 15 | 2000 | 1.9 | 4 | 4 | 114,9 | 3/4 |
| 16 | 2000 | 2.5 | 3 | 4 | 119,2 | 3/4 |
| 17 | 2000 | 2.5 | 4 | 4 | 116,7 | 3/4 |
| 18 | 2000 | 2.5 | 5 | 4 | 113,4 | 3/4 |

*Semi dry samples*

**Table 60. Plasma parameters for semi dry samples where the dispersion was sprayed on to the fabric.**

| Sample | Plasma parameters | | | |
|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between the electrodes [mm] | No. of cycles |
| 1 | 1200 | 2.5 | 3 | 4 |
| 2 | 1200 | 2.5 | 4 | 4 |
| 3 | 1200 | 2.5 | 5 | 4 |
| 4 | 1600 | 2.5 | 3 | 4 |
| 5 | 1600 | 2.5 | 4 | 4 |
| 6 | 1600 | 2.5 | 5 | 4 |
| 7 | 2000 | 2.5 | 3 | 4 |
| 8 | 2000 | 2.5 | 4 | 4 |
| 9 | 2000 | 2.5 | 5 | 4 |

**Table 61. Contact angles for semi dry samples where the dispersion was sprayed on to the fabric.**

| Sample | Contact angle(Left, Right angle)[°] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | | 2 | | 3 | | Average value | Standard deviation |
| 1 | 124,9 | 125,1 | 72,4 | 76 | 113,7 | 115,3 | 104,566667 | 24,0184651 |
| 2 | 54,9 | 56,6 | 105,9 | 105,5 | 117,8 | 117,8 | 93,0833333 | 29,4253915 |
| 3 | 75 | 79,9 | 91,4 | 90,2 | 58,9 | 60 | 75,9 | 14,1658745 |
| 4 | 75,1 | 78,5 | 78,6 | 78,6 | 87,1 | 87,2 | 80,85 | 5,06152151 |
| 5 | 67,1 | 70,3 | 86 | 86,3 | 100,4 | 100,2 | 85,05 | 14,194189 |
| 6 | 57,6 | 62,7 | 0 | 0 | 75,3 | 82,3 | 46,3166667 | 36,9351549 |
| 7 | 81 | 75,5 | 130,6 | 131,3 | 105,6 | 105,2 | 104,866667 | 23,6372305 |
| 8 | 122,4 | 123 | 104,1 | 103,9 | 102,5 | 101,9 | 109,633333 | 10,1570993 |
| 9 | 114,9 | 115,3 | 104,4 | 104 | 120,9 | 120,2 | 113,283333 | 7,45155465 |

## Dispersion No .4

**Table 62. Plasma parameters for sprayed sample, that were left to dry for 2h in R.T before plasma treatment.**

| Sample | Plasma parameters | | | |
|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | Number of cycles |
| 1 | 1200 | 2.5 | 3.3 | 4 |

**Table 63. Contact angles for sprayed sample.**

| Sample | Contact angle(Left, Right angle)[°] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | | 2 | | 3 | | Average value | Standard deviation |
| 1 | 119.2 | 118.8 | 133.6 | 133.7 | 123.1 | 123 | 125.2 | 6.76776674 |

Körde sedan ett test med enbart C-6 som sprayades på med en blomvattnarspray.

## Dispersion No .5

**Table 64. Plasma parameters, contact angles and oil repellency of dry samples (left to dry in R.T for 3 days before being plasma treated) that were sprayed with dispersion No 5. Also a reference sample that was treated the same way but with no plasma treatment.**

| Sample | Plasma parameters | | | | Results | |
|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) |
| Reference | - | - | - | - | 139,5 | 8 |
| 1 | 1600 | 2.5 | 1 | 2 | 118,3 | 6 |
| 2 | 1600 | 2.5 | 1 | 3 | 123,9 | 6 |

**Table 65. Plasma parameters, contact angles and oil repellency before and after Martindale (2000 cycles against wool fabric at 12 kPa) of dry samples (left to dry overnight at R.T before being plasma treated) that were sprayed with dispersion No 5. Also the results for a reference samle that was treated in the same way but with no plasma treatment.**

| Sample | Plasma parameters | | | | Results | | |
|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) | Oil rep. after 2000 cycles in Martindale |
| Reference | - | - | - | - | 139,4 | 8 | 4/5 |
| 1 | 1600 | 2.5 | 1 | 3 | 108,4 | 6 | 4 |
| 2 | 1600 | 2.5 | 1 | 3 | 141,2 | 8 | 4/5 |

Sample 1 was sprayed before the plasma treatment and sample 2 was sprayed with AM-95 after the plasma treatment.

## Dispersion No .6

**Table 66. Plasma parameters, contact angles and oil repellency before and after Martindale (2000 cycles against wool fabric at 12 kPa) of dry samples (left to dry overnight at R.T before being plasma treated) that were sprayed with dispersion No 5. Also the results for a reference samle that was treated in the same way but with no plasma treatment.**

| Sample | Plasma parameters | | | | Results | | |
|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) | Oil rep. after 2000 cycles in Martindale |
| Reference | - | - | - | - | 142,4 | 6 | 4 |
| 1 | 1600 | 2.5 | 1 | 3 | 112,0 | 5 | 2 |
| 2 | 1600 | 2.5 | 1 | 3 | - | 6 | 3 |

Sample 1 was sprayed with S-11 WS before the plasma treatment and sample 2 was sprayed after the plasma treatment.

## Dispersion No .7

**Table 67. Plasma parameters, contact angles and oil repellency before and after Martindale (2000 cycles against wool fabric at 12 kPa) of dry samples (left to dry over night at R.T.)**

| Sample | Plasma parameters | Results | | | | | |
|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Average Contact Angle [°] | Oil repellency (Highest liquid passed) | Oil rep. after 2000 cycles in Martindale |
| 1 | 1200 | 2.5 | 1 | 3 | 90,7 | 2 | 2 |
| 2 | 1600 | 2.5 | 1 | 3 | 88,1 | 2 | 2 |
| 3 | 2000 | 2.5 | 1 | 3 | 92,5 | 3 | 2 |

## Dispersion No .8

**Table 68. Plasma parameters and oil repellency before and after Martindale (2000 cycles against wool fabric at 12 kPa) for dry samples (immersed in dispersion, calendered and left to dry at R.T over night).**

| Sample | Plasma parameters | | | | Results | |
|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Oil repellency (Highest liquid passed) | Oil rep. after 2000 cycles in Martindale |
| 1 | 1600 | 2.5 | 1 | 3 | 0/1 | - |
| 2 | 4000 | 2.5 | 1 | 3 | 2 | - |
| 3 | 6000 | 2.5 | 1 | 3 | 2 | 1 |

**Table 69. Plasma parameters, oil repellency and spray tested dry samples (immersed in dispersion, calendered and left to dry at R.T over night).**

| Sample | Plasma parameters | | | | Results | | |
|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Pickup [g AFR6 / g Dry fabric] | Oil repellency (Highest liquid passed) | Spray test grading |
| 1 | 1600 | 2.5 | 1 | 3 | 0,0199 | 1 | 1 |
| 2 | 1600 | 2.5 | 1 | 6 | 0,0205 | 1 | 1 |
| 3 | 2000 | 2.5 | 1 | 3 | 0,0200 | 1 | 1 |
| 4 | 2000 | 2.5 | 1 | 6 | 0,0203 | 1 | 1 |

## Dispersion No .9

**Table 70. Plasma parameters, oil repellency and spray test for dry samples (immersed in dispersion No 9, calendered and left to dry over night before being plasma treated).**

| Sample | Plasma parameters | | | | Results | | |
|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Pickup [g AFR6 / g Dry fabric] | Oil repellency (Highest liquid passed) | Spray test grading |
| 1 | 4000 | 2.5 | 1 | 2 | **0,0208** | 1 | 1 |
| 2 | 4000 | 2.5 | 1 | 4 | **0,0220** | 1 | 1 |
| 3 | 4000 | 2.5 | 1 | 6 | **0,0210** | 2 | 1 |
| 4 | 1600 | 2.5 | 1 | 3 | **0,0209** | 0 | 1 |
| 5 | 4000 | 2.5 | 1 | 2 | **0,0202** | 0 | 1 |
| 6 | 4000 | 2.5 | 1 | 4 | **0,0209** | 2 | 1 |

**Table 71. Plasma parameters, oil repellency and spray test for dry samples (immersed in dispersion No 9, and left to dry over night (without any calendaring) before being plasma treated).**

| Sample | Plasma parameters | | | | Results | |
|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Pickup [g AFR6 / g Dry fabric] | Oil repellency (Highest liquid passed) |
| 1 | 1600 | 2.5 | 1 | 3 | **0,0289** | 1 |
| 2 | 1600 | 2.5 | 1 | 4 | **0,0359** | 1/2 |
| 3 | 2000 | 2.5 | 1 | 3 | **0,0331** | 1 |
| 4 | 2000 | 2.5 | 1 | 4 | **0,0356** | 2 |

**Table 72. Plasma parameters, oil repellency and spray test for dry samples (immersed in dispersion No 9, calendered and left to dry in R.T over night before being plasma treated.**

| Sample | Plasma parameters | | | | Results | | |
|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Pickup [g AFR6 / g Dry fabric] | Oil repellency (Highest liquid passed) | Spray test grading |
| 1 | 1600 | 2.5 | 1 | 3 | 0,0202 | 1 | 1 |
| 2 | 1600 | 2.5 | 1 | 4 | 0,0198 | 1 | 1 |
| 3 | 2000 | 2.5 | 1 | 3 | 0,0195 | 1 | 1 |
| 4 | 2000 | 2.5 | 1 | 4 | 0,0206 | 0 | 1 |

## Dispersion No .10

**Table 73. Plasma parameters, oil repellency and spray test for dry samples (immersed in dispersion No 10, calendered and left to dry in R.T over night before being plasma treated.**

| Sample | Plasma parameters | | | | Results | | |
|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Pickup [g AFR6 / g Dry fabric] | Oil repellency (Highest liquid passed) | Spray test grading |
| 1 | 1600 | 2.5 | 1 | 3 | 0,0540 | 1 | 1 |
| 2 | 1600 | 2.5 | 1 | 4 | 0,0518 | 2 | 1 |
| 3 | 2000 | 2.5 | 1 | 3 | 0,0516 | 1 | 1 |
| 4 | 2000 | 2.5 | 1 | 4 | 0,0525 | 1 | 1 |

**Table 74. Plasma parameters and oil repellency for dry samples (immersed in dispersion No 10, calendered and left to dry at R.T. over night before being plasma treated with argon gas)**

| Sample | Plasma parameters | | | | Results | | |
|---|---|---|---|---|---|---|---|
| | Power [W] | Speed of the frame | Distance between electrodes [mm] | No. of cycles | Pickup [%] | Pickup [g AFR6 / g Dry fabric] | Oil repellency (Highest liquid passed) |
| 1 | 1600 | 2.5 | 1 | 4 | 46,903 | 0,0469 | 2 |
| 2 | 1600 | 2.5 | 2 | 4 | 46,429 | 0,0464 | 2 |
| 3 | 1600 | 2.5 | 3 | 4 | 45,614 | 0,0456 | 2 |
| 4 | 1600 | 2.5 | 4 | 4 | 46,018 | 0,0460 | 2/3 |
| 5 | 2000 | 2.5 | 1 | 4 | 46,491 | 0,0465 | 2 |
| 6 | 2000 | 2.5 | 2 | 4 | 46,903 | 0,0469 | 3 |
| 7 | 2000 | 2.5 | 3 | 4 | 46,018 | 0,0460 | 2 |
| 8 | 2000 | 2.5 | 4 | 4 | 46,491 | 0,0465 | 2 |

# Calculations for pickup

There were two equatons used when calculating the pickup:

$$Pickup\ \% = \frac{Rolled\ weight\ of\ the\ fabric - Dry\ weight\ of\ the\ fabric}{Dry\ weight\ of\ the\ fabric} \qquad Eq. 3$$

$$\frac{\text{Mass Chemical [g]}}{\text{Mass Fabric [g]}} = \frac{(Rolled\ weight\ fabric - Dry\ weight\ fabric) \times Weight\ Chemical}{Total\ weight\ of\ chemical\ bath\ (Diluent + Chemical) \times Dry\ weight\ fabric} \quad \text{Eq. 4}$$

Calculating the Pickup % for sample 1 in table 74:

Dry weight of the fabric = 11.3 g

Rolled weight of the fabric = 16.6 g $Pickup\ \% = \frac{16.6-11.3}{11.3} = 0.46903 = 46.903\ \%$

Calculating mass chemical per mass fabric for sample 1 in table 74:

Total weight of chemical bath (Table 7 , Dispersion 10) = 400 g

Weight chemical (Table 7, Dispersion 10) = 40 g

$$\frac{\text{Mass Chemical [g]}}{\text{Mass Fabric [g]}} = \frac{(16.6-11.3)\times 40}{400 \times 11.3} = 0.0469\ \frac{\text{g chemical}}{g\ frabric}$$