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Corona and dielectric barrier discharge plasma treatment of textiles for technical applications

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5.1 Introduction to atmospheric-pressure plasma processes

Growing demands on the functionality of technical textiles as well as on the environmental friendliness of finishing processes increase the interest in physically induced techniques for surface modification and coating of textiles. In general, after the application of water-based finishing systems, the textile needs to be dried. The removing of water is energy intensive and therefore expensive. In contrast to conventional wet finishing processes, a plasma treatment is a dry process. The textile stays dry and, accordingly, drying processes can be avoided and no waste water occurs. Plasma treatments represent, therefore, energy efficient and economic alternatives to classical textile finishing processes. Within plasma processes, a high reactive gaseous phase interacts with the surface of a substrate. In principle, all polymeric and natural fibres can be plasma treated.

For many years, mainly low-pressure plasma processes have been developed for textile plasma treatment. However, the integration of these processes, which typically run at pressures between 0.1 and 1 mbar, into continuously and often fast-running textile production and finishing lines is complex or even impossible. In addition, due to the need for vacuum technology, low-pressure processes are expensive.

The reasons why plasma processes at atmospheric pressure are advantageous for the textile industry are in detail:

- The typical working width of textile machines is between 1.5 and 10 meters. Textile-suited plasma modules need to be scalable up to these dimensions, which is easier for atmospheric-pressure techniques.
- Textiles have large specific surfaces compared to foils, piece goods or bulk solids. Even with strong pumps, the reduced pressure which is necessary for low pressure plasma will only be reached slowly due to the desorption of adsorbed gases.

- Depending on the fibre material, textiles can adsorb and absorb relatively large amounts of water. To reduce the chamber pressure below the vapor pressure of water (23.4 mbar at 20 °C), a drying process is necessary. This is time consuming because diffusion processes within the fiber and the cooling due to evaporation of the water slow down the drying (vapour pressure of ice: 4.02 mbar at –5 °C). The evaporation time can be shortened by heating the substrate.
- Atmospheric-pressure processes can be combined with spraying or aqueous aerosols.
- Atmospheric-pressure processes are in-line capable, in contrast to batch low-pressure plasma processes.
- Investment and maintenance costs for atmospheric-pressure plasma modules are moderate.

New markets can be opened if plasma processes that have been developed for low-pressure conditions so far are transferred to normal pressure conditions.[1] The dielectric barrier discharge (DBD) process belongs to those plasma processes that can also be applied at atmospheric pressure. Therefore, research efforts are being made over many years, with cooperation between partners from textile and plasma research institutes and industry, in order to make DBD technology a useful and practicable method for the textile industry, aiming at the development of new products, improved textile functions and sustainable processes.[2,3]

A focus of ITV Denkendorf, within its research and development projects, are new technologies for continuous plasma coating of wide fabrics under atmospheric pressure and the improvement of the profitability of the plasma coating processes. For example, oil and water repellent layers are deposited on the substrate and new processes are opened up by combining plasma treatments with sprayed aerosols.

Only low-temperature discharges can be used in order to functionalise textiles by plasma treatment.[4] In low-temperature plasmas, the thermal energy of the neutral atoms and molecules stay roughly at room temperature; however, the free electrons can transmit high energy. So the electrons have to be heated to a minimum of 10 000 K, while the gas temperature, which is controlled by the thermal energy of atoms and molecules, remains at moderate temperatures. These plasmas can interact with the polymer surface for some milliseconds without thermally changing the substrate. In thermal plasmas, however, the neutral particles are in thermal equilibrium with the charged particles and transmit too much energy to the polymer surface, which instantly destroys the textile. Flame treatment as thermal plasma is common in textile processing; however, this technology is mainly used for the removing of the hairs of textiles – not for functionalisation.

Functionalising is a chemical process. Thereby, the reaction time of the reaction partner is an important process parameter. This means for a plasma treatment, the longer the polymer surface is exposed to the activated reactive gas, the more functional groups are formed, and within limits the better is the desired effect.

5.1.1 Corona discharge

In material processing practice, the term 'corona discharge' is often understood differently from the term in physics and electronics. Strictly speaking, corona discharge occurs if a rather asymmetrical electric field has an effect in a gas causing electric current to flow in a range between μA and mA. The considerable inhomogeneous field needed for this is typically reached by an asymmetrical shaping of the electrodes. The simplest electrode configuration consists of a metallic needle opposite a conductive plate, or of a thin wire within a metallic cylinder.

If the metallic needle or the wire, respectively, is connected to the negative pole of a power supply and the large, extensive electrode (plate and cylinder, respectively) is connected to the positive pole, a negative corona discharge occurs. In the reverse case of polarity, a positive corona discharge is the result.[5] Corona discharge differs from glow discharge (weak current) and arc discharge (high current) with respect to the flow of current. Within a corona discharge, the current varies over a wide range and is mainly caused by charge carriers of only one polarity. The electric field mainly concentrates at the highly curved electrodes. Therefore, light emissions occur in a negative corona at this cathode region. Most of the gap between the electrodes remains dark, however. This so-called 'drift zone' is occupied by negatively charged particles. In this area, the charge carriers are decelerated by permanent collisions between the gas particles and slowly drift towards the electrode. In the glowing region of high electric field strength, the charge carriers can receive enough kinetic energy between two collisions with gas particles to transmit sufficient energy to fragmentise, ionise or set the collision partners in strong molecular vibration. If electrons are excited by the collision to energetically higher states, light quantums can be emitted when the electrons reoccupy the lower energy level.

In the case of a negative corona, electrons are generated in the strong electrical field at the curved electrode. These electrons are accelerated within the field and transfer their energy to surrounding gas particles. Subsequently, they are taken up by neutral particles in the dark drifting zone and form negative ions, which slowly drift towards the large and positively charged anode.

In the case of a positive corona, no electrons can be set free at the cathode. In the drifting zone the electric current is practically carried only

by positive charge carriers. When they impinge on the cathode, they cannot – in contrast to the negative corona – eject new electrons from the electrode. Negative charge carriers in the drifting zone can be generated only by photoionisation or natural radioactivity. These can only cumulatively multiply in the area of very high field strength near to the positively charged, needle-like electrode. Under similar external conditions, the positive corona discharge is inhibited, in contrast to the negative corona discharge. The discharge current is halved.

The typical field strengths for corona discharges are roughly around 40 and 50 kV/cm at radii between 2 and 10 mm. Discharge currents range between μA and mA. A typical corona discharge current is below 200 μA.[6]

Such 'real' corona discharges are used for textile treatment in order to either remove or to specifically apply electrostatic surface charges from or to fabric layers, but not for surface functionalisation or activation. The electrostatic discharge of fabric layers is, for example, advantageous in the case of hydrophobic fibres such as PP-nonwovens or textiles finished with fluorocarbons. Due to friction and contact with non-grounded surfaces, surface charges can occur which exert strong, long-reaching coulomb forces on fabrics, thus, for example, preventing proper plaiting. The charged fabric, moreover, tends to attract dust particles. Normally, dust is not quite neutral but slightly negatively charged so that dust particles whirled up by air flows are directed to the textile surface by positive charges and adhere due to electrostatic forces. If the fabric layer is discharged, the dust particles can be sucked off. In the textile industry, re-damping by aerosols is improved by electrostatic charge.[7] Textile webs and yarns with the same electric charges repel each other, thus avoiding blocking.

In the case of fabrics and webs processed at high velocities, a gas boundary layer is coupled to the surface. Corona discharge helps to convert this layer from a laminar to a turbulent flow. This facilitates the drying process of the web as the steam is transported, along with the fabric, in the laminar boundary layer. As a turbulent flow, the humid layer can more effectively be sucked off from the fabric.[8,9] The prerequisite for switching a flow from laminar to turbulent, however, is that the flow is already relatively close to instability. This means that the discharge process is not able to cause any turbulence over slowly moving surfaces. This technology is distributed by the company Eltex (EFD-technology). Corona discharge can further be used in order to effectively exchange the air entrapped within a textile and to substitute it by inert or reactive gas. It has been shown that the efficiency in the discharge-supported exchange of oxygen by nitrogen within a fast running web increases with the web velocity. Sixty-three per cent of the entrapped oxygen was washed out by nitrogen at 55 m/min web speed, whereas at 150 m/min web velocity, 86% of the entrapped oxygen was exchanged by nitrogen.[10,11]

5.1.2 Dielectric barrier discharge

The set-up for dielectric barrier discharge processes, although similar to the corona discharge, has characteristic deviations from the corona set-up. The most important characteristic is that at least one electrode is coated completely by an insulator, the dielectric barrier for electric currents.

The Dielectric Barrier Discharge (DBD) belongs to the class of non-equilibrium low-temperature plasmas. The DBD is characterised by high energy of the free electrons, while the ions and neutral particles gain only little additional kinetic energy. Kinetic energy and momentum is transferred to the particles upon collision with electrons which have been accelerated along the electric field lines. Because of their low weight and small collision cross-section, the electrons gain considerably more thermal energy compared to the heavy and large gas particles. Upon collision between the fast electrons and gas molecules or atoms, the molecules are fragmented or transferred into electronically excited highly reactive states.

The formation of a dielectric barrier discharge process is complex and will be described only in basic detail here. First an electric field is created. Free charge carriers are accelerated by coulomb forces in this field. Even a very few free electrons from a natural source such as cosmic radiation or natural radioactivity are sufficient to initiate a discharge process. These charge carriers are accelerated within the field and generate new ion-electron-pairs upon collision with neutral gas particles. Mainly the light electrons are accelerated and absorb thermal energy. Additional electrons are emitted into the gas gap upon the impact of ions on the electrode. The avalanche-like generated cloud of charge carrier moves towards the positively charged electrode. The characteristic light emissions within the visible and UV-range of plasma discharges result from collision-induced electronically excited states of the gas atoms and molecules. The electric field between the counter electrode and the charged cloud becomes stronger, while the field between the negatively charged electrode and the cloud breaks down. At the time the electron cloud reaches the positively charged electrode, the complete high voltage is applied at the dielectric electrode coating and the gas gap is field-free. No currents can flow any longer and the discharge is extinguished, although the whole gas gap is still electrically conductive. This breakdown process of initiation, avalanche-like charge carrier generation, and extinguishing happens within a few nanoseconds. However, dependencies with the kind of gas, gas gap size, gas pressure and nature of the dielectric coating exist.

The DBD is so-called 'filamented'. At normal pressure, many single-discharge filaments, also called streamers, are generated within the gap between the electrodes in spatial and temporal random distribution over

the length of the gap. The individual discharge filaments do not interact with each other apart from the initial electron generation by UV-radiation. One filament has a radius of around 0.1 mm and transports an average electric current of 0.1 A. The average electron energy ranges between 1 and 10 eV. The dissipated amount of energy per filament is in the range of microjoules. A discharge that hits the dielectric layer of the counter electrode generates a so-called footprint – an area where the charge is distributed on the dielectric surface by sliding discharges. The footprint is a few square millimetres in size and is considerably larger than the discharge filament diameter.[12–14] These surface discharges also occur on the surfaces of textile fibres, which are located within the discharge gap. These surface discharges enhance the effect of the DBD with respect to a fibre surface functionalisation because reactive species are generated exactly at the fibre surface where they are needed for the reaction process.

Dielectric barrier discharge is the most commonly applied technology in order to achieve an easily up-scalable, expanded, non-equilibrium plasma for the treatment of wide webs and fabrics. The free electrons in the plasma discharge are heated up to 10 000–100 000 K while the gas itself can be kept at moderate temperatures, typically between room temperature and 100 °C. This allows the treatment of textiles without thermal damaging of the fibrous substrate. The ambient air is often used as a process gas in a DBD because of its easy availability and the reactivity of the oxygen. The molecular oxygen in the air can be converted into reactive atomic oxygen radicals or excited ozone molecules.

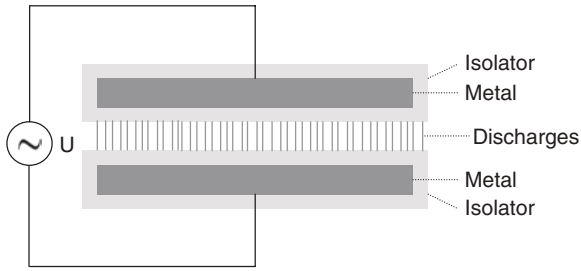
The set-up for DBD processes is typically characterised by the combination of two opposing electrodes with an intermediate mm-sized air gap. At least one electrode is coated by an insulator. The dielectric barrier covers the whole surface of the electrode and acts as an isolating barrier for electric currents. The dielectric layer needs to be resistant to high voltages of a few kV. It has to suppress electric currents even when the high voltage is applied. Only negligible currents through the barrier are allowed. Local avalanche breakdowns through the barrier may not occur. The electrode arrangement of the barrier discharge acts like several condensers in series, with different capacities and dielectric strengths, within an electric circuit. The gas gap forms the condenser, which leads to the avalanche breakdown within the gap when a sufficiently high voltage is applied. A spark develops and the condenser is temporarily discharged, caused by the electrically conductive plasma. The electric current which flows during the discharge is obstructed by collisions with and between gas particles. The gas forms a resistor, which transfers energy into the gas. The dielectric coatings of the electrodes inhibit an uncontrolled current such as an arc discharge between the electrodes. Only alternating currents can pass the condenser while

direct currents are blocked. In order to repeatedly or almost continuously couple power to the discharge, a DBD must be run with alternating currents. A second discharge at the same site can only take place when either the voltage has been doubled or when the polarity sign has been inverted. The common frequencies range between 1 and 100 kHz. The excitation frequency depends on the resonance frequency of the oscillating circuit, which is formed by the transformer coil, electrode gap and dielectrics. Relatively high power can be coupled to the plasma if frequencies are excited that are close to the resonance frequency. Frequencies that deviate significantly from the resonance frequency can couple only little power into the system.

At the minimum ignition voltage, the discharge ignites only at an especially favourable point. If the electrodes, for example, are not quite plane-parallel to each other, the site with the smallest gap is the preferred site for the first discharge. If the voltage is increased, more discharges are generated side-by-side at other sites, which fill the whole gap between the electrodes with a discontinuous plasma.

The technical term dielectric barrier discharge has been established in the textile and foil processing industries for the above-described processes. However, in practice, processes with discharge by commonly only one dielectric layer and preferably in air are also often called corona discharge. This is technically speaking not correct, because dielectric barrier discharges fundamentally differ from corona discharges. Both, corona discharges and DBD are so-called silent discharges but in contrast to the DBD, corona discharges have an extensive dark field and are generated between two highly asymmetrically formed metallic electrodes. The coating of at least one of the two electrodes by a high-resistant dielectric barrier practically prevents the operation under conditions of direct current. At corona arrangements, low-resistant barriers can prevent an arc discharge and distribute direct current equally to many point electrodes. The electrical current at each electrode is quite often limited by an inserted protective resistor. In dielectric barrier discharge, however, highly-resistant coatings such as glass, ceramics or silicone rubber (PDMS) are used, whose electrical conductivity can practically be neglected. The total high voltage must be applicable to the barrier layer without leading to avalanche break-down events.

One reason for the misuse of the corona term is that, in many cases, a considerably asymmetrical electrode configuration is chosen for barrier discharges of fabrics or foils. The fabric is directed over a broad roller which forms one often grounded electrode. The high-voltage bar-shaped electrodes are arranged around the roller, parallel to the roller axis; however, they are small compared to the radius of the roller. This results in the following definition of dielectric barrier discharge DBD:



5.1 Principle of dielectric barrier discharge.

A dielectric barrier discharge (DBD) is a filamented discharge between two electrodes with at least one dielectric, with a high frequency excitation, mostly in the range between 1 and 100 kHz (Fig. 5.1).

The traditional and most common application of corona and DBD technology, respectively, is the improvement of wetting of non-polar surfaces. Such low-energy surfaces, which are typical for polymeric materials, have poor wetting properties with regard to polar, high surface tension liquids. A high surface tension liquid such as water or water-based dispersion only spreads and forms a stable film on surfaces with comparable high surface tension. On non-polar, polymeric surfaces, aqueous films will break and dewet, forming single, isolated droplets. A stable film formation is important for printing, varnishing, coating and several other applications. DBD treatment often helps to avoid these dewetting phenomena by increasing the surface energy. The advantages of DBD treatment are better wetting and better adhesion of the printed dyestuff or lacquer to the treated substrate. This positive effect of DBD treatment is also used in combination with glue. Hot-melt, reactive adhesive and water-based adhesive layers have an improved peel adhesion on plasma functionalised polymers.

The DBD process is especially of use for applications with roll-to-roll systems with thermally sensitive materials such as foil, textiles or photographic print paper. But DBD is used to alter other materials such as wood, insulated cable or even fingernails. The benefits of DBD with regard to technical textiles are described in more detail later.

5.2 Special adaptations of DBD technology to textiles

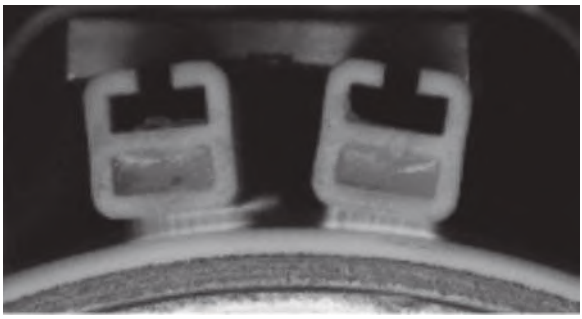
The potential of surface modification of roll goods by corona discharge technology has been known for a long time and has been established in areas such as the foil industry.[15] However, attempts to use the same technology for textile treatment usually failed.[16] This is because the corona treatment of foils has been usually performed with a set-up of metallic electrodes. A polymeric foil, though usually a non-porous electrical insulator, then acts

as a dielectric barrier between the electrodes. The foil forms either a dielectric barrier on one electrode if it is in tight contact to the electrode and the discharge filament end is on the surface of the foil, or two separate discharges occur if there are gaps between the foil and both electrodes. Thus, a corona treatment of foils has, in effect, many characteristics of a dielectric barrier discharge. Problems with the corona treatment of textiles occur because textiles differ from foils in many aspects – textiles are commonly thicker than foils and have an inhomogeneous structure. They are porous and gas permeable and typically very rough, even hairy. Their specific surface area is much larger than those of foils. Therefore, textiles cannot inhibit the penetration of the discharge as do foils. Discharge streamers can pass through the textile along the electric field direction, at least locally. These filaments are high-current, hot discharge streamers because the gap between the electrode has to be wide according to the thickness of the textile and no dielectric barrier on the electrodes limits the current in the corona set-up. The high current flow along the yarn surface through the textile can induce carbonisation of the polymer. Even minimal carbonisation increases the local electrical conductivity of the substrate permanently. This, however, results in a subsequent concentration and localisation of further discharges at this point, damaging the textile increasingly. The typical results are micro-fine holes within the substrate.

In paper finishing, this effect of micro-perforation is partly used in order to generate specific properties such as improved air permeability or different filtering behaviour.[17] Textiles, however, are considerably more inhomogeneous than paper and it is hardly possible to control the process towards well-directed perforation via corona discharges.

Since textile perforation is commonly an undesired result, the aim of textile plasma treatment is to achieve a discharge that is as homogeneous as possible. The surface functionalisation should take place as effectively as possible and be as gentle as possible for the substrate. This aim can be reached by different modifications to the established corona technology. Several combinations of metal, silicone-, glass- and ceramic-coated electrodes have already been tested for the treatment of textiles. It turned out that the use of only one dielectric – as it is meanwhile common for foil treatment with a dielectric-coated roller – is not sufficient for the treatment of textiles. Textiles can be better treated by means of two dielectric-coated electrodes. This is because, via two dielectric barriers, the electric current distributes into more single filament discharges thus making the discharge pattern more homogenous (Figure 5.2).[9]

It is further recommended to select a discharge gap as narrow as possible. This is because, with increasing distance, the breakdown voltage rises and the size of the footprints as well as the current of a single discharge increases. High local currents, however, can damage the textile. Accordingly,



5.2 Dielectric barrier discharge between ceramic-coated electrodes.

voltage must be adapted to the dimension of the discharge gap and the textile to be treated. So, the shorter the electrode distance, the lower is the necessary breakdown voltage and the lower is the current in the single filament. A narrow gap facilitates a homogeneous coupling of power to the discharge.

It is further found that textiles usually need to be treated at much lower substrate velocity than foils to gain comparable and satisfactory results. This is because textiles have a much larger specific surface than foils, due to their fibrous structure. In order to generate a surface density of functional groups comparable to foils, it is necessary to generate considerably more reactive sites. Furthermore, in textiles, the filaments of a yarn are closely packed, thus obstructing the exchange of gases. Therefore, textiles must be exposed to a plasma for a longer time compared with foils, in order to compensate both disadvantages, the large surface area and the reduced accessibility of the activated plasma gases to the fibre surface. This can be best attained by reducing the fabric-speed or by scale-up, arranging more electrodes in sequence.

Modifications of the electrode configuration are helpful as well. A more symmetric electrode assembly is advantageous for textile treatment. This is because an equal number of discharge filaments is generated during each half wave of the alternating potential of the electrodes when the electrodes are symmetrically assembled. Each discharge in each direction during each half wave carries approximately the same current, enhancing the overall homogeneity of the discharge.

Intermitting of the excitation frequency is another suitable tool to make the DBD more homogeneous. Intermittation means to electronically switch the generator on and off according to a given pulse-break ratio. This enables one to control the coupling of power independently of the applied voltage. Intermitting mode can be of further advantage for rather slow plasma activated reactions. Reactive gases, e.g. for plasma polymerisation, can be fed

into the plasma zone during a break. Chemical processes can continue during the break, thus saving unnecessary energy.

The results of DBD treatments of textiles from natural fibres, e.g. wool or cotton, and also man-made fibres, have been frequently published. Significant changes of textile properties such as friction coefficient, surface energy or improved antistatic behaviour have been reported.[5–7]

5.2.1 Principal chemical processes in DBD systems and aspects of heating

The chemical processes that are initiated in the plasma are usually very complex and depend on the chemical species in the gas gap. In synthetic air alone ($O_2 + N_2$), more than 100 reaction paths and some 30 different species must be considered in order to understand the processes within a DBD. The gaseous molecules are excited and partially fragmented ready to react with a partner in a chemical reaction. Positive ions are generated upon collision with high energy electrons, whereas the capture of slow electrons leads to the formation of negatively charged ions. These charge carriers, however, are only short-lived and disappear within approximately 50 ns after the initialisation of the discharge process.

Nitrogen and oxygen, as main components of air, are the most important collision partners of the accelerated electrons, if the DBD is performed with air as plasma gas. Generated neutral radicals such as $O(^3P)$ and $O(^1D)$ as well as $N(^4S)$ and N(D) react with surface molecules or with molecular oxygen in different electronic states O_2, $O_2(A)$, $O_2(a)$, $O_2(b)$ and nitrogen N_2, $N_2(A)$ to more stable intermediate products such as O_3^* or NO or NO_2. The excited ozone disappears after approximately one millisecond, while stable ozone remains. Nitrogen monoxide is converted after the discharge into different nitrogen oxides – N_2O, N_2O_5, N_2O_3 and NO_3 – within the tenth of a second.[9] Hazardous gases such as ozone, which are typically generated within a DBD in air, need to be exhausted, disposed of or destroyed, e.g. with activated carbon filters, in order to guarantee workplace safety.

In order to generate a streamer discharge in air, the breakdown field strength of 27 kV/cm must be exceeded. The actual voltage to be applied also depends on the nature of the dielectric barrier.

Apart from oxygen and nitrogen, real air does also contain water, CO_2, hydrogen and rare gases, all of which are involved in the reaction mechanisms. Rare gases such as argon, however, are not really inert in a plasma, because they can transfer energy and even be converted into short-lived, energy-rich molecules, so-called 'excimers'.

Although the DBD is a so-called 'cold discharge', the electrodes will become hot with time. A control over the electrode temperature by cooling of the electrodes can be necessary for different reasons:

- First, after a typical DBD-treatment over several hours, the temperature of the electrodes will rise to between 100 and 200 °C. The textile properties are likely to be changed by thermal stress. Textiles which remove heat insufficiently, e.g. due to low web speed, can display increased brittleness or changed colour.
- Second, plasma processes are temperature dependent. If, for example, a polymer layer is to be deposited in the plasma, heat might impede the polymerisation and deposition. On the other hand, moderately heated electrodes can support a hydrophilic treatment of textiles in air. A plasma regime change can be observed in air when the temperature approaches 80–100 °C. In the case of hot electrodes, the discharge is more homogeneous and less filamented than with cold electrodes. The coupled power decreases measurably switching from cold to hot electrodes, while the voltage remains constant. It is supposed that the change of the plasma regime goes along with the stability of ozone; the plasma generated ozone becomes unstable when the temperatures exceed 80 °C. It is assumed that it is mainly the enforced decay of ozone that causes the observed regime change. More oxygen atoms are generated, which are available for the surface modification, thus accelerating the process to impart hydrophilic properties to the fabric.

The aim, therefore, is an efficient adjustment of temperature and cooling of the system to achieve optimal treatment results for continuous DBD operation. This can be efficiently reached by cooling the electrodes.

5.2.2 Technical possibilities of DBD technology

Fabrics such as woven fabrics, knitted and warp knits, nonwovens, laid fabrics, papers and foils, as well as mono and multifilaments, staple fibre yarns, roving yarn, carded nonwovens but also single fibres and powders, can be treated with the described method of dielectric barrier discharge. Limitations or specific configurations are, for example, necessary for electrically conductive textiles. In a common DBD set-up, the endless substrate should be an electric insulator. Otherwise it is likely that electric currents flow along the substrate to the grounded parts of the machine that it is in contact with, such as grounded deflection rollers. High current discharges between the textile and the grounded element might occur, which might damage the substrate.

A specific tandem DBD set-up has been described to treat electrically conductive substrates potential-free. The set-up consists of two symmetrically arranged pairs of electrodes. They are electrically controlled in a way that a filament-like discharge occurs between the first electrode and the substrate. The discharge current flows along the substrate to the second

discharge zone. The filamented discharge at this plasma zone closes the electric circuit.[18]

5.3 Plasma-induced surface activation of fibres

Plasma surface activation is usually understood as a plasma treatment under non-polymerising conditions. The chemical surface modification is initiated by radical reactions of the plasma-activated gases or plasma-generated UV-irradiation without a layer deposition. In atmospheric pressure plasmas, the surface activation typically takes place with oxygen-containing gas mixtures such as air. Surfaces with low functionality become more reactive by enhancing the concentration of oxygen-containing or other polar groups at the surface. Activation can also mean the increased wettability of surfaces whose surface energy is increased by the polar surface groups.[19] Surface energy is an important characteristic value, especially for wettability by aqueous systems.

5.3.1 Applications of DBD treatment in technical textiles

For many, particularly technical, applications of the textiles, strong adhesive bonds between the textiles and other substrates are needed. Thus, bonding, coating or laminating are important working steps. They are responsible for efficient processing and sustainable functionality of the product. Problems in the assurance of durable adhesion to textile substrates have many causes. The flexibility of a textile poses a specific challenge for adhesive bonds. On the fibers, residues from processing agents like spin finish or sizing agent, which originate from the previous manufacturing steps, prevent good adhesion to fibre surfaces. But even a pure surface of a synthetic fibre such as polyester (PET), polyacrylonitrile (PAN) or highly drawn polyolefine has a crystalline and hydrophobic character. Wettability and chemical reactivity of synthetic fibres are therefore usually poor and adhesion forces are weak.

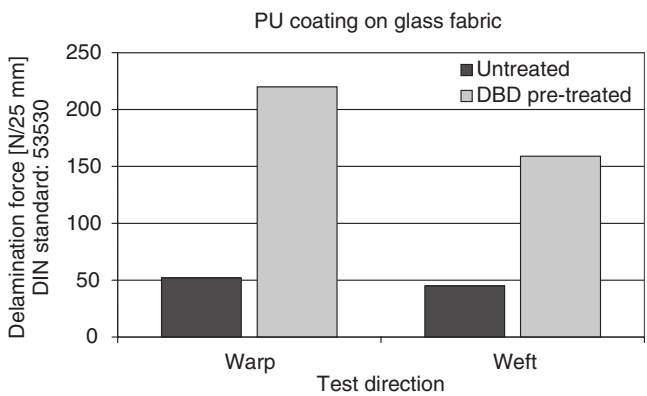
In the following, the potential of DBD treatments to improve the adhesion of coatings and bondings to other substrates will be demonstrated by practical examples. In all cases, the subsequent processing of the plasma-treated textiles has taken place following a period of at least a few hours after the DBD treatment. This evaluates the practicability of the process because it has to be tolerant to short storage times and typical delays in the manufacturing process. Due to this waiting period, it is assumed that, at the time of processing of the plasma treated textiles, no short-lived reactive functions such as unsaturated radicals exist any more on the fibre, but polar, oxygen-containing groups are the basis for the observed adhesion effects.

For the practical tests, mainly polyurethane coatings were applied to different textile substrates. Due to their elastic and film-forming properties, polyurethanes are an important material class for coating and bonding of textiles. Although solvent-based polyurethanes are still processed in a few instances, in most cases water-based polyurethane dispersions are used. An improved wetting of the textiles by these dispersions should result in improved adhesion. For example, DBD-treated and non-treated polyester fabrics have been PU-coated using a water-based polyurethane dispersion. After drying and curing, the delamination force, measured by peel tests, was found to be 50–200% higher on the plasma pre-treated than on the non-activated fabric, depending on the dose.

As a second example, two polyester fabrics have been bonded to each other by a direct processed polyurethane film. Peel tests proved that the adhesion force could be enhanced many times over a non-activated sample by plasma pre-treatment, depending on plasma dose.

A DBD pre-treatment significantly improved, even with glass fabrics, the adhesion of a polyurethane coating that was applied by transfer coating. For both warp and weft direction, the delamination forces of the coating increased by a few hundred per cent (Figure 5.3). In addition to the better adhesion performance, the plasma pre-treated material was much more resistant to hydrolysis than the non-activated fabric and, even after 90 days of immersion in water only few signs of delamination could be found.

DBD pre-treatment is not only effective with regard to water-based coatings and glues. For example, co-polyamide hot-melts were coated onto a polyester multifilament fabric at a critical low processing temperature, with usually poor resultant adhesion performance as measured by a peel test according to DIN 53357. As another example, to improve the adhesion of a seam-sealing tape, the top charmeuse layer of a three-layer laminate for



5.3 Enhanced adhesion performance of coatings by plasma activation of the fabric.

functional clothing was DBD pre-treated. The adhesion force of the tape was measured by a peel test according to DIN 53530. In both cases, the hot-melt and the tape, the adhesion force was found to be doubled compared with non-pre-treated fabrics.

Other applications of plasma activation of textiles have enhanced water pick-up and intensified and improved dying results with pre-treated textiles.

5.3.2 Mechanism of surface activation

Important steps during an air-plasma treatment of polymers are exemplarily described below for polyethylene. A carbon–hydrogen bond gets cleaved by either electron impact, photo effect or energy transfer from an excited atom or molecule. The released hydrogen radical is removed by diffusion or chemical reaction. A single occupied unstable and high reactive sp^3-orbital remains at the carbon atom. This radical site can react fast with an oxygen molecule, forming a peroxy radical. Alternatively, the secondary radical can be stabilised by additional hydrogen separation in the neighbourhood, resulting in carbon–carbon double bonds or stable allyl radicals. The fast reaction of the alkyl radical with oxygen is preferred with regard to a possible reaction with nitrogen because oxygen molecules have a radical character. The generated peroxy radical at the polymer chain can be transferred into a hydroperoxy function by separating a hydrogen atom from a neighbouring carbon atom. This can initiate a chain reaction because the newly generated radical can react with an oxygen molecule on its part. By this mechanism, a radical site can migrate along a polyethylene chain. The hydroperoxy groups are not endlessly stable but will be converted into stable oxygen-containing groups such as carbonyls or carboxyls. In contrast to the initial hydrogen functions, these oxygen functions have increased polarity. Polar liquids can interact with the polar surface groups by long-reaching electrostatic forces. With increased density of polar surface groups, the surface energy grows and polar liquids such as water can more easily wet the material and spread over the surface.[20,21]

The described reaction mechanisms had been confirmed by X-ray photoelectron spectroscopy (XPS). By XPS, the relative frequency of atoms in the top surface layer and their specific states of chemical bonds can be measured. For example, the ratio of oxygen to carbon can be determined, which can be used to prove the significantly increased oxygen concentration on air-plasma treated polyethylene or polypropylene surfaces.[22]

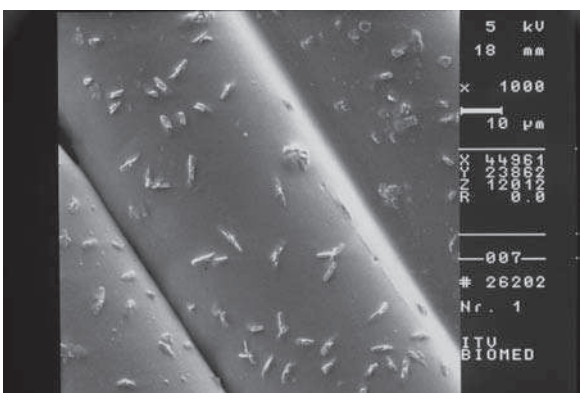
The duration of the plasma treatment is of importance. In general, the longer the plasma treatment lasts, the more oxygen can be chemically bound to the surface. Although the surface energy might not change any further after a specific treatment time, a prolonged plasma treatment will

delay a decay of the effect after stopping the exposure. However, the plasma treatment should be run as short as possible not only for economic reasons; a long plasma treatment can also damage the fibrous substrate.

A plasma source always emits UV radiation. Some UV sources are even based on dielectric barrier discharges. In contrast to the plasma-generated particles, the UV radiation can penetrate deeply into the bulk substrate. A scission of chemical bonds can be the result, which might reduce the tear strength of the fibre.

It has also been observed that oligomers accumulate at the surface of plasma-treated polymers after long exposure. Oligomers are short fragments of polymers with approximately 10–30 repeating units. The oligomers are either generated directly at the surface or migrate from lower layers to the surface, by diffusion. The oligomers are non-reactive and have only weak adhesion to the substrate and therefore spoil the effectiveness of a plasma treatment. Plasma-induced degradation of polymers (Figure 5.4) can often be detected by scanning electron microscopy, showing increased roughness of a former smooth surface. But already a covering of the surface by oligomers can affect adversely the adhesion of coatings.[23–25]

The previously described example of improved coating of plasma pretreated glass fabrics (Section 5.3.1) reveals the importance of improved wettability of the textile substrate by the liquid or paste-like coating in order to improve its adhesion. Any unspecific chemical surface modification that increases the surface energy is likely to raise the adhesion strength of coatings. In the case of glass fabrics, the plasma treatment probably does not chemically modify the glass fiber itself but organic residues on the glass fibre. This is likely because the relatively low electron energies between 1 and 8 eV within dielectric barrier discharges are sufficient to break covalent bonds such as C—H and C—C, but they are not sufficient to break the



5.4 Surface degradation of a plasma-treated polyurethane yarn.

strong Si—O bonds of the glass. The improved adhesion of coatings on DBD-treated glass fabrics can be explained by hydrophilic modification of hydrophobic spin finishes and sizing residues on the glass yarns. The water-based dispersion can penetrate deep into the yarn and the coating can enclose every single fibre. The contact area between textile and coating is raised and the tight fit is better. Delamination forces can be transferred to larger surface areas. Beside the local delamination and detachment of the coating from the fibre, cohesive fracture within the coating or glue is enforced.

This differentiates the plasma-activated bonding and coating of textiles significantly from the pre-treatment of foils or non-porous substrates in general. For those non-porous materials, a chemical modification of the polymeric substrate by reactive functions which support a covalent bond between polymeric substrate and coating is essential. The existence of short-lived reactive sites such as radicals are crucial for improved adhesion to foils, while for porous textiles an improved wettability can be the major reason for better adhesion. Thus, the subsequent processing of plasma-treated textiles can still be possible after storage over days or even weeks because the plasma-induced hydrophilisation is stable over those periods for many substrates. However, the post-processing of plasma-activated textiles should occur as soon as possible to benefit most from the activation and the existence of short-lived reactive functions.

5.3.3 Stability of DBD-treatment effects

It is a common observation that the chemical and physical activity of plasma activated polymeric surfaces diminishes with time. Although the chemical bonds that are generated by the plasma treatment are stable, the effect of a raised surface energy or chemical reactivity is not endlessly durable. This ageing of the surfaces is of specific relevance for polymers with low glass transition temperatures. Materials such as polypropylene or silicones have very high polymer chain mobilities. They age rather fast and the effects of plasma activation are often lost after a day of storage under normal conditions.[26–28] The explanation for this phenomenon is seen in the fact that the high surface energy condition of a plasma-treated polymer is an energetically unfavoured metastable state. A reorientation of polar molecules to each other and a migration of unpolar groups to the surface results in an energetically favoured state, where the polar groups are buried within the bulk and are therefore ineffective. If the polymer has large amorphous fractions at the surface, or the glass transition temperature is low, such reorientations can take place soon after the surface modification. Due to this mobility-based effect, high diffusion rates and storage at elevated temperature will accelerate the ageing process.

XPS analysis of air-plasma treated surfaces over a long time demonstrates the loss of even chemically stable functional plasma-induced groups with time. The oxygen/carbon ratio at the surface slowly decreases without the presence of potential reaction partners and under normal conditions that exclude a chemical reduction of the oxygen containing groups.[22]

The ageing of plasma-induced surface activation effects does strongly depend on the material. It can be diminished by cross-linking the activated surface, which can result from the plasma treatment as well. If the surface becomes cross-linked by breaking and recombining of chemical bonds, the chain mobility is decreased and the stability effect increases.

Very stable plasma activation effects can, on the other hand, be observed with polar or crystalline polymers such as cotton or polyester (PET). In experiments air-DBD-treated cotton warp yarns have remained hydrophilic over at least 3 weeks and activated polyester felts kept their plasma induced hydrophilicity over 2 years of storage.

Beside the influence of the pure fiber polymer, the durability of a plasma treatment depends also on usage conditions and other chemical parameters. Because the plasma modification only affects a very thin, monomolecular top layer, the effect is always modified by friction and abrasion. Polymeric additives also might have influence on the effect and stability of plasma treatments, as well as spin finishings, sizing agents and other functional finishing agents. If they cover the whole fibre, only those finishing agents will be modified by the plasma treatment.

5.4 Deposition of nano-layers by gas polymerisation

Plasma treatments of textiles are not limited to relatively unspecific activations of the textile surface. The gas within the discharge controls the discharge behaviour as well as the formation of reactive species. If reactive gases that are able to polymerise after excitation in the discharge are fed into the plasma zone, thin coatings can be deposited on the substrate from a non-equilibrium plasma by, for example, radical polymerisation.

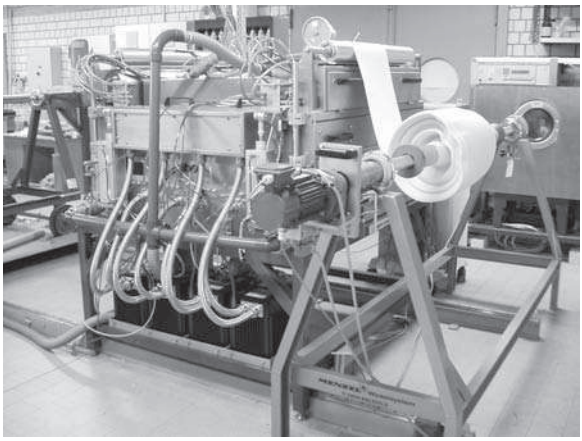
The morphology of the coating and the deposition rate are controlled by the reaction mechanism and reaction rate. Readily polymerising systems form particles within the discharge, which can be deposited on the substrate. However, for textile treatments, these dust-forming plasmas are less relevant because the particles typically lie loosely on the surface.

Of much higher interest are polymerisation processes which predominantly take place at the substrate surface, forming a permanent functional surface coating. For example, highly cross-linked layers with varying surface energies, depending on the chemical composition, can be deposited from non-equivalent plasmas:

- C—H—O-containing layers with compositions $C_{0.6–0.75}$ $O_{0.01–0.05}$ $H_{0.2–0.35}$, formed in hydrocarbon atmospheres generate surfaces with surface energies between 45 and 56 mN/m.[29]
- From organosilicone-containing atmospheres, SiO_2-like coatings with surface energies up to 66 mN/m as well as low energy silicone-like layers with 30 mN/m can be created.[22]
- Coatings with very low surface energies can be generated with gaseous fluorocarbon precursors. PTFE-like surfaces are very hydrophobic because their surface energy lies below 20 mN/m. Responsible for the plasma polymerisation of fluorocarbons and the efficient formation of PTFE-like layers is the bi-radical and reactive fragment CF_2. This polymerisable molecule results from the discharge-initiated fragmentation of fluorocarbons. Together with other fragments such as CF_3 or CF, a highly cross-linked polymeric coating can be deposited via surface reactions on the substrate.[7,22]

For plasma coating processes, the plant design needs to be more complex than the relatively simple constructed surface-activation modules. Compared with the one-step surface activation process, plasma polymerisation is a slow multi-step process. The polymeric chain growth is initiated by fragmentation in the plasma and completed by polymer and network formation at the surface of the substrate. Therefore, to create a functional polymeric surface layer of adequate thickness from gaseous monomers, a sufficient residence time of the precursors and the substrate within the plasma zone is needed in order to form the activated monomers, transport them to the surface, and carry out the surface polymerization. Beside plasma residence time and plasma energy dose, the layer-forming plasma processes also depend on reaction processes occurring without or outside the plasma discharge. Because of this, a pulsed plasma source is of advantage for the plasma polymerising processes.[30]

Open plasma devices as are typically used for continuous surface activation of webs are not suited for plasma polymerisation. In order to define and control the necessary gas composition in the reaction zone accurately, and even to be able to run the plasma process under exclusion of air components (oxygen or nitrogen free), an encapsulation is necessary. In Figure 5.5, a device for plasma coating of textile webs is shown. The prototype has been designed to fulfil both the demands of the academic and industrial developer for efficient process development and the textile industry for industrial use. Salient features are easy loading and unloading, integration into an in-line coating line, treatment widths of 1 m, up-scale possibilities, various modules for monitoring and varying the gas balance, and separate control of all electrodes. A simply designed in- and outlet module for the



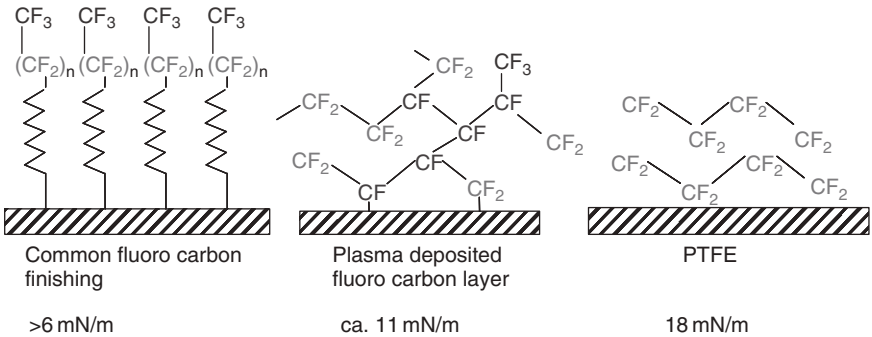
5.5 Enclosed device for continuous plasma coating of up to 1 m wide webs.

textile, acting as a gas lock to remove air fractions from the textile before entering the plasma chamber, even allows a continuous in-line roll-to-roll processing of textiles.

5.4.1 Hydrophobic and oleophobic treatment by DBD

The generation of water- and oil-repellent functional layers on textiles by plasma polymerisation of fluorocarbons at atmospheric pressure under continuous in-line conditions has been a major issue in collaborative research projects at ITV Denkendorf.[31]

The structures of plasma polymerised fluorocarbon coatings are characterized by a relatively high degrees of cross-linking, which can be deduced from CF-group detection by XPS-analysis.[32] The molecular structures and specific chemical functionalities of the used gaseous precursors are only rudimentarily found in the cross-linked deposited layer. The surface energies strongly depend on the density of CF_3-groups at the fluorocarbon surfaces. Schematic structure models of common fluorocarbon textile finishings, PTFE and plasma polymerised fluorocarbons in Figure 5.6 illustrate this. The highest degree of oil repellence can be achieved with perfluorinated side group functionalised resins. With ideally arranged CF_3 groups, the surface energy can be decreased down to 6 mN/m. On the other side, since PTFE contains no CF_3 functions but only CF_2 groups, PTFE has a higher surface energy, approximately 18 mN/m, which is insufficient for oil repellence on textiles. For the formation of plasma-generated oil-repellent fluorocarbons, the choice of precursors and the process parameters have to be



5.6 Schematic structure models of different fluorocarbon surfaces.

optimised so that both an efficient CF_2-based layer formation and a densely CF_3-functionalised surface are realised.

XPS analysis of plasma generated fluorocarbon layers show the need for a precise and continuous control of the atmosphere within the reaction chamber and the plasma zone in order to achieve reproducible and effective polymerisation processes. The plasma polymerisation of fluorocarbons is markedly sensitive towards even small amounts of oxygen in the plasma zone. With oxygen concentrations above 1%, the oxygen in the deposited coating is increased at the expense of a decreased fluorine content, which significantly lowers the oil repellence of the treated textile.[33,34]

With the current state of the art of plasma polymerisation of fluorocarbons at atmospheric pressure, surface energies of 11 mN/m on foils have been achieved. These are significantly lower than the typical 18 mN/m for PTFE. After treating textiles by plasma polymerisation of economical, market-available fluorocarbons at atmospheric pressure under continuous in-line conditions, good oil repellence could be detected.

In two trials (i) a polyester monofilament fabric, treated at a velocity of 0.5 m/min, proved to be oil-repellent Grade 5-6 according to the AATCC 118-1992 standard. (However, the effectiveness of common water-based fluorocarbon resins – oil repellence Grades 7–8 after application – has not been reached so far.) (ii) a fluorocarbon plasma treatment of a hydrophilic fabric of texturized polyester/polyamide yarn (90 g/m^2) reduced the water absorption and water retention properties of the fabric by 60–70%.

The hydrophobic and oleophobic fluorocarbon plasma-generated coatings are stable. On a plasma-treated polyester felt the oil repellence was found to consistent over the measurement period of 9 months and beyond.

5.5 Combination of DBD treatment and liquor deposition

The use of aerosols within plasma processes is restricted to atmospheric pressure plasmas but widely expands the number and kind of suited chemicals for atmospheric plasma processes. By means of aerosols, chemicals that are liquid at atmospheric pressure, solutions, or even dispersions, can be used in combination with a plasma process for surface functionalisation.

5.5.1 DBD systems in combination with aerosols

Systems for DBD treatment in combination with aerosols are commercially available, such as the *AS Coating Star* module of the company Ahlbrandt System (Figure 5.7). This system contains one or more aerosol generators and a specific electrode housing with an aerosol inlet in addition to the common ceramic-coated roller and bar electrodes. The aerosol-generating nebulisers are positioned directly in front of the electrode housing and generate, by means of pressurised gases, e.g. air or inert gases, floating levitated aerosols from usually aqueous solutions, with an average droplet diameter below 1 μm. 1 ml aerosol solution equals $2 * 10^{12}$ (2 trillion) droplets of 1 μm diameter. These droplets are directed, with the nebuliser gases and additional transport gases, through a system of slot dies into the plasma zone. The amount of aerosol is controlled by the gas flow of the nebuliser gases while the volume flow of the transport gases regulates the velocity of the gas/aerosol phase entering the discharge region. The gas–aerosol ratio

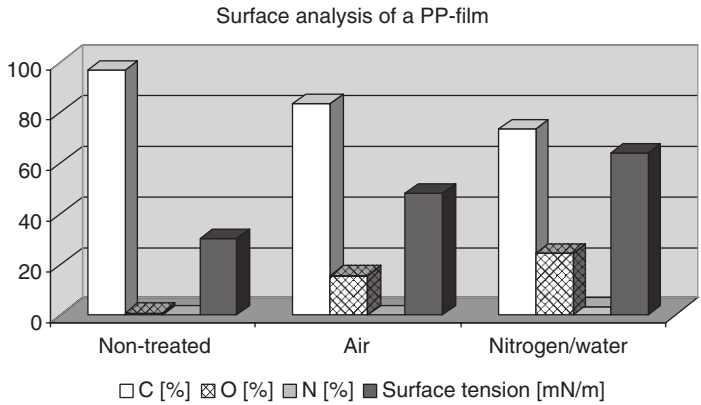
5.7 Corona system with eight nebulisers for aerosol application.

can be adjusted at the same time. Depending on the temperature of the heatable nebulisers, the maximum output of aerosols is 200 ml/h per nebuliser. The regulation of the aerosol throughput is first of all controlled by the number of nebulisers within the system, beside the gas flow regulation. A typical number of nebulisers is 1–10 per 1 m working width. The viscosity of the fluids should be below 100 mPa s. If possible, only solutions should be used. The use of dispersions has to be checked in every case and only nm-scaled dispersed particles can be considered. Because of these boundary conditions, the concentration of functional additives is between 1 and 10% in most cases. This determines the amount of applicable substances. Depending on the web velocity, the maximum substance application lies between 1 and 100 mg/m^2.

It is advantageous to make the slot dies exchangeable and freely positionable. The aerosols can then be applied either outside the discharge in front of or behind the electrodes, or directly into the discharge between the electrodes. It depends on the aimed functions whether it is better to choose a nozzle position that applies the aerosols to the substrate before it enters the discharge or after leaving the discharge, or to a position that injects the aerosol into the most active plasma zone. Feeding of the aerosols behind the electrodes avoids fragmentation and destruction of functional substances, as well as undesired layer deposition on the electrodes. Such a configuration is suited for anti-static or anti-microbial finishings. The application of simple, commercially available, non-toxic, water soluble polymers results in anti-bacterial properties with partially very high durability.

This method of gas/aerosol application is, in general, best suited for substances that are effective also in low concentration. The necessary effective dosage of the functional additives limits the maximum web velocity. Depending on the textile application, web speeds are below 10 m/min.

An injection of the aerosol into the most active discharge zone allows plasma-activated reactions. The discharge characteristics are strongly influenced by the concentration and kind of the induced substances. In this configuration, it is possible that the high-voltage electrodes become unintentionally coated. This contamination might degrade the plasma efficiency. Such problems are avoided by a process which uses water aerosols in a nitrogen atmosphere in order to achieve exceptionally high surface energies. The electrode temperatures of above 150°C let the water droplets quickly evaporate. In the resulting homogeneous plasma discharge, the molar fraction of water in the plasma atmosphere can be very high. Such a plasma achieves a much higher surface energy on polyolefines or polyester compared with simple barrier discharges in air with the same corona energy. Besides a better wettability, the treated surface also demonstrates better adhesion of subsequent coatings, which can be explained by a higher density of functional groups at the substrate surface (Figure 5.8).



5.8 Comparison of surface properties (atom content on surface measured by XPS and surface energy measured by test inks) of an untreated polypropylene foil, a PP-foil treated in standard air-DBD and a PP-foil treated in nitrogen-DBD in combination with a water aerosol.

The very high fraction of oxygen containing groups on the water/nitrogen–aerosol–plasma-treated polypropylene surface has to be explained by the water fraction in the plasma atmosphere being the only significant oxygen source, because the oxygen concentration within the nitrogen/water plasma is below 1%. While barrier discharges in air primarily result in a generation of peroxy functions on the substrate by activating O_2 molecules, a discharge in nitrogen/water atmospheres creates mainly OH-functions. Without any other additives, plasma-activated pure aqueous aerosols avoid undesired coating of the electrodes, making this process configuration free of maintenance.

5.5.2 Current developments for improved DBD use and effectiveness

The operational costs of atmospheric pressure plasma processes are strongly influenced by the kind and consumption of the used gases. The most economic option is a discharge in air or a combination of air discharge with liquid aerosols. However, as discussed above, this process is limited to small quantities of applicable substances. Therefore, other application systems which can apply larger substance quantities, as are for example necessary for hydrophobic treatment at higher web velocity, are currently under development.

The use of nitrogen is the most economic option for oxygen-free or inert gas based atmospheric-pressure plasma processes. Depending on working

width and web velocity, a typical nitrogen consumption lies between 10 and 100 m^3/h. A significant cost reduction can be achieved by re-feeding the used nitrogen. Such recirculation devices are already developed and have to be tested in continuous operation.

If textiles are to be treated continuously by a continuous oxygen-free or inert gas based plasma treatment, the gas locks at the plasma chamber entrance and exit need specific attention. The undesired entrainment of oxygen or other air fractions by the substrate into the chamber and the discharge gap rises proportionally to the volume and the web velocity of the textile. While for treatments of foils and flat substrates the oxygen entrainment is independent of the substrate, for textile treatments the specific textile properties play an important role. A test series is necessary for each substrate to adjust each parameter in order to stay within the tolerances of acceptable remaining oxygen concentrations.

An alternative to the very fine aerosol producing nebulisers are spraying devices that use fast rotating discs. The generated droplets are bigger than 1 μm and larger quantities of liquid substances can be applied. An enclosed 1 m pilot plant at ITV Denkendorf is equipped with such a spraying device. Due to its principal and required space, this spraying device cannot be placed very close to the discharge region. However, water-based textile finishing agents can be applied immediately after the activation of the textile in the dielectric barrier discharge.

It will need further R&D efforts to tap the full potential of a combination of aerosols from nebulisers or spraying modules with the dielectric barrier discharge for surface functionalisation of textiles. Examples for current and future developments are:

- physical surface modification, e.g. to generate electret properties
- chemical functionalisation
- minimal application and energy efficient finishing processes
- chemical and topographical nano-structuring.

5.6 Future trends

Plasma systems that allow the surface treatment of substrates independent from substrate porosity, area size and topography will be of specific interest for the processing of textiles. Systems that are independent of the position of a counter electrode seem capable of this. In conventional systems, for example, the maximum substrate thickness is limited by a maximum discharge gap between electrode and counter electrode. Systems with so-called indirect or remote plasma sources are able to penetrate into thick textile substrates and homogeneously modify three-dimensional structures. A

special challenge is the design of an adequate plasma system for the typical wide working width of textiles.

5.6.1 Developments in discharge technologies

Low-pressure plasma treatments for surface functionalisation and coating have a broad field of application in the processing of semiconductors, optical and medical devices and machinery manufacturing.

Non-thermal atmospheric-pressure plasma technologies have led a shadowy existence beside the corona treatment of polymeric surfaces. However, in recent years it has been shown that a number of non-thermal processes, even CVD processes, which were limited to low pressure plasmas, could be successfully transferred to the atmospheric pressure range. Starting points were the plasma technical developments of individual plasma sources such as Dielectric Barrier Discharge, arc-jet, microwave and hybrid plasma sources. The new plasma sources are generally usable for surface modification, substrate pre-treatment, surface cleaning, etching and plasma chemical coating.

Compared to plasma spraying and other thermal plasma treatment techniques, the advantage of non-thermal atmospheric-pressure plasma techniques is the possibility of coating large surfaces of heat-sensitive substrates such as textiles with nano-scale functional layers.

The treatment width of such plasma systems varies widely, starting at a few millimetres (coplanar discharges, jets). These plasma sources can be scaled up to larger treatment width by arranging arrays of single sources. Surface patterning can be realised by structuring dielectrics via print-like methods generating hollow discharges.

Two systems can be differentiated in the field of atmospheric-pressure plasma deposition processes:

(i) Precursors, either gaseous or as aerosols, are applied directly into the discharge gap where the plasma is generated. Plasma chemical deposition of fluorocarbons and silicon oxide layers have been realised on pilot plant scale.
(ii) By means of remote processes, the plasma generation and the activation zone of the precursors are separated. Deposition rates of 100 nm/s are possible.[35]

5.6.2 Developments in computer simulation

The on-going expansion of fundamental knowledge about the generation and effect of plasmas, in combination with further evolving software and hardware for numerical simulations, are the bases of simulations of the

chemical/physical processes of plasma treatments. Numerical simulations can support the optimised design of plasma devices with regard to gas flow, electrical modules and effect.

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6

Nano-scale treatment of textiles using plasma technology

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6.1 Introduction

This chapter highlights the aspect of nano-scaled treatments of textiles in different ways. Briefly, plasma technology can be used for ablation and deposition processes. While ablation enables a complete cleaning of textiles from manufacturing residuals, deposition can be controlled in the nanometre range to achieve new functionalities. The textile properties remain unaffected with both treatments and they are dry and eco-friendly processes. Section 6.2 thus shows some advantages of plasma technology for the textile industry besides looking at the gain from nano-size (dimension of 10^{-9} m). Section 6.3 deals with materials and methods with respect to the pressure range (atmospheric or low pressure plasma) and plasma reactors. Section 6.4 examines the effectiveness of plasma cleaning, focusing on fabrics, fibres, and the scale-up of the presented methods. Sections 6.5 and 6.6 are similarly organised, considering plasma metallisation and plasma polymerisation, respectively. They investigate the special requirements for fabrics and fibers to achieve nano-scaled coatings, as well as the transfer to industrial-size processes (scale-up). 'Plasma co-polymerisation' (Section 6.7) describes a combination of sputtering and plasma polymerisation to obtain nano-particles within a polymeric matrix. The benefit of this new approach is outlined. 'Future trends' (10.8) and 'Further information' (10.9) complete the chapter.

6.2 Plasma technology for the textile industry

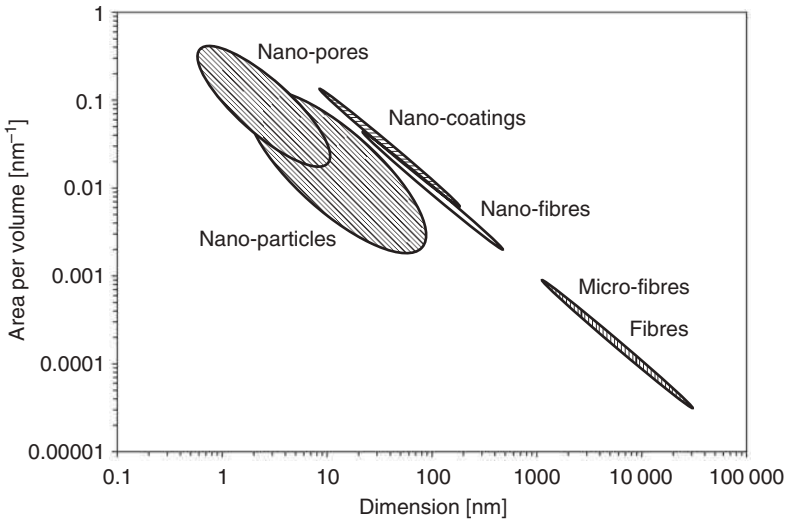
The challenges the textile industries of Europe and North America are facing today are enormous. Therefore, the need for a reorientation is strong. In order to survive, the transition to a knowledge-based economy focusing

on high-value added products is needed. Plasma technology offers an attractive way to add new functionalities to textiles, such as water and stain repellence, hydrophilicity, conductivity, biocompatibility as well as new or improved mechanical, optical and tribological properties.

The plasma state consists of an equal part of negatively and positively charged particles (quasi-neutrality), excited states, radicals, metastables and vacuum ultraviolet (VUV) radiation. Surface treatments of materials can be performed by non-equilibrium plasmas, which are excited by electric fields. Since the energy coupling is conducted by electrons, which achieve a mean temperature of several electron volts (corresponding up to 100 000 K), the main part of the plasma-activated gas remains close to room temperature. The electrons, however, gain just the right energies to excite, dissociate and ionise atoms and molecules. The degree of ionisation typically lies between 10^{-4} and 10^{-6}. The reactive plasma particles and radiation yield a nano-scaled interaction with material surfaces by chain scission and cross-linking reactions, radical formation, etching or deposition. The bulk properties of materials can thus be maintained. Textiles and fibres differ from other materials mainly by their complex structure showing openings at different length scale (micro- to nanometre range) such as filament or interfibre distances, resulting in higher surface areas.

An important characteristic of the nano-scale (1 nm = 10^{-9} m or a millionth of a millimetre) is also the increasing surface area with respect to the bulk material. Hence, surface sensitive processes strongly benefit from nano-technology. This effect is already used for micro-fibres, since their fineness improves, for example, wicking and softness. Nano-fibres showing even higher areas per volume are used, for example, for air filtration. The deposition of nano-scaled coatings on textiles, starting at several nanometres in thickness to obtain a complete coverage of the textile surface, can provide a high surface functionality, e.g. for adhesion or wettability improvement, while using a low amount of material. Nano-particles embedded in a surface layer or a coating are used for drug release and photo catalytically active or anti-microbial interfaces. Their area per volume ratio also depends on the density of the nano-particles within a matrix and their size distribution. Nano-porous coatings containing a high amount of accessible functional groups show the highest area per volume ratio, which depends on porosity, for pore sizes around 1 nm (Figure 6.1). These coatings are of high interest for their dyeability and as anti-fogging or non-fouling surfaces.

Using plasma technology to modify textile surfaces, etching and deposition reactions can be used to obtain nano-particle or nano-porous structures. Moreover, it is a dry and eco-friendly technique, avoiding waste production as found in wet-chemical processes. However, for the transfer into industry, both the feasibility of scale-up and economic aspects have to be regarded.



6.1 Surface area per volume depending on the size of different structures. The area per volume is proportional to the inverse length scale (diameter of fibres, thickness of coatings, size of particles and pores). The density of the nano-particles is taken as 5 to 50% and the porosity of the nano-porous coatings as 10 to 40%.

6.3 Materials and methods

In principle, all types of textile materials may be treated within a plasma (Kang, 2004a, b). Considering the nano-scaled treatment of textiles using plasma technology, however, the special geometry, manufacturing residuals (sizes) and additives, as well as the water content, have to be taken into account. The structure of the considered textile will show several dimensions, including the filament distance and the interfibre (yarn) distance, as well as contacting areas or protruding fibre ends. Thus, different treatment conditions due to different incident angles of reactive particles and shadowing effects can be expected for different fibre surface areas, complicating a homogeneous treatment. The mean free path (pressure), the lifetime (reaction probability) and the width of the plasma sheath surrounding the substrates determine the type of active particles that might reach the substrate surfaces and contribute to the treatment. Manufacturing residuals might cover the entire fibre surfaces, requiring a cleaning step prior to the plasma functionalisation of textiles. Moreover, desorption from textiles as well as etching or sputtering products might substantially change the plasma gas composition. Outgassing of textiles also yield a more intense VUV radiation by H_2, H_2O, and CH gas desorption (Wertheimer, 1999).

In the following, we mainly consider textile fabrics and fibres as examples for two different textile geometries. However, knitwear, non-wovens, paper or membranes can be treated analogically to fabrics.

6.3.1 Pressure range

The pressure range selected for textile treatments using plasma technology strongly influences the achievable functionalisation effects, but determines also the required plasma equipment (Hegemann, 2006a). For the textile industry, mainly plasma systems running under atmospheric pressure seem to be of interest, to enable a continuous process. Corona discharge treatment in air, used industrially since the 1950s, still represents a major process for surface activation of polymers, textiles, and other flexible substrates of simple geometry. Corona discharges, operated at high voltage in the 10–20 kHz frequency range, however, are not homogeneous, for they consists of filamentary microdischarges yielding hot spots and damaging textile surfaces. Alternative methods, such as atmospheric pressure Dielectric Barrier Discharges (DBD), on the other hand, lose some of their advantages such as a high process velocity, and encapsulation is required to obtain the more or less defined gas composition required for more advanced plasma treatments. Furthermore, the textile structure hinders the penetration of reactive particles due to low mean free path lengths. Contrary to atmospheric plasmas, low pressure discharges contain energetic particles, long-living radicals, and vacuum ultraviolet (VUV) radiation due to longer mean free paths. Especially, long-living oxygen and hydroxyl radicals formed in low pressure plasmas are able to penetrate into open structures in the micrometre or sub-micrometre range that are found in textiles and membranes (Oehr, 2005; Kull, 2005).

Mainly by the variation of the pressure, the plasma process can be optimised for different treatments and textile structures. Moderate pressure plasmas (100 to 1000 Pa) were found to give optimum cleaning and activation conditions with non-polymerisable gases since a high number of active particles contribute to chemical etching (Poll, 2001; Keller, 2005). Plasma polymerisation can best be controlled using low pressure plasmas (1 to 100 Pa), due to well-defined plasma zones (Hegemann, 2006a). In this pressure range, the mean free path lengths are high enough to allow the penetration of the textile structure by energetic particles and long-living radicals. Good conditions for plasma polymerisation are thus enabled on textile fibres up to several fibre layers in depth, such that external media interact with the treated fibres. Sputtering processes, finally, are carried out in the pressure range between 0.5 and 5 Pa to avoid in-flight scattering collisions of the background gas and the sputtered atoms (Rossnagel, 2003). Therefore, at the authors' institute (Empa), mainly low-pressure plasmas are considered to obtain nano-scaled treatments on textiles.

6.3.2 Plasma reactors

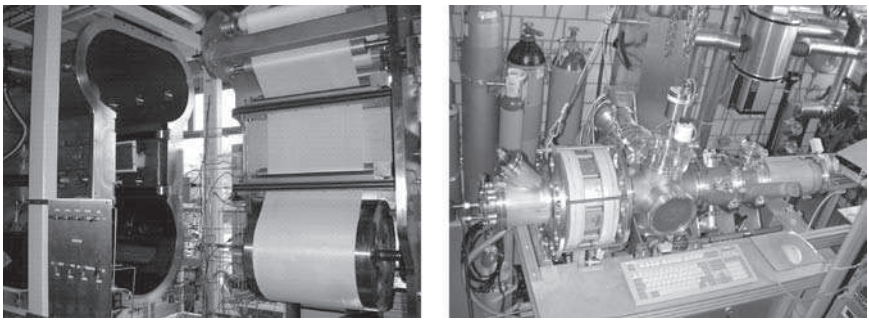
To build a reactor for plasma polymerisation on textiles, a vacuum chamber is required to enable low-pressure plasma processes. In a vacuum it is easier – at least when different types of textile fabrics, non-wovens, membranes, and papers are to be treated – to have the winding inside the chamber, enabling a semi-continuous treatment. Obviously, this kind of process cannot be integrated directly into a production line.

Large reactors for low-pressure plasma treatments on textiles are available. Plasma excitation in the kilohertz range (typically 40 kHz) is mainly used for industrial purposes due to lower costs. Radiofrequency (RF) or microwave (MW) sources are also applicable, if required by the process. The reactors are typically designed for textile widths up to 120 cm: larger widths (up to 4 m) are possible. The reactors are loaded with textile materials, closed, evacuated and run in a semi-continuous process from reel-to-reel. The textiles are led through the plasma regions adapted to the required process, which comprises usually a cleaning and a plasma deposition step.

To avoid some limits of plasma polymerisation on fabrics or other webs (huge reactor, semi-continuous process, fibres contacting other fibres), the direct treatment of fibres is also of importance. One advantage of fibre processing is the possibility to perform unwinding (before plasma treatment) and winding (after plasma treatment) in air by leading the fibres through suitable openings into the low pressure region using a differentially pumped sealing system. A modular set-up by the combination of separated plasma chambers enables different process steps such as plasma pre-treatment (cleaning), deposition, and post-treatment. Flexible textile fibres, yarns, etc. can be run several times through the plasma zones, enhancing the plasma length and thus the process velocity. Furthermore, different treatment times that might be required for different process steps such as cleaning, deposition, and post-treatment can thus be adapted for a one-step processing. In-line production is achievable by process velocities as high as several hundred metres per minute. Therefore, both a (semi-continuous) web coater and a (continuous) fibre coater are present at Empa (Figure 6.2), which serve as pilot-plant reactors to demonstrate industrial scale-up.

The large web coater admits reel-to-reel processing of webs up to a width of 65 cm and a velocity of 100 m/min (corresponding to a treatment time of a few seconds). Three separated treatment zones allow pre-treatment, coating, and post-treatment in one process step. A large drum (62 cm in diameter) in the lower chamber provides a deposition area of around 2 m in length. Depositions can be performed via plasma polymerisation and/or magnetron sputtering.

The unique fibre coater is equipped with an inverse cylindrical magnetron enabling the uniform coating of fibres or wires (Amberg, 2004). Additionally,



6.2 Empa's plasma reactors for web coating (left) and fibre coating (right).

plasma treatment and plasma polymerisation processes can be performed. The fibres are wound and unwound in air and are transported through a sealing system into the vacuum chamber. Velocities up to 100 m/min can be reached with fibre diameters ranging from micrometres to millimetres. Automatically controlled pumping systems using rotary, roots and turbomolecular pumps enable a fast evacuation of the reactor chambers down to a pressure of 10^{-3} Pa.

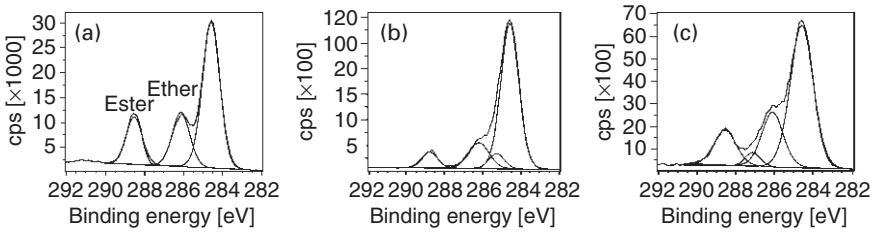
Additionally, batch reactors with different geometries and excitation sources (RF, MW and magnetron sputtering) are used for the optimisation of plasma processes.

6.4 Plasma cleaning

During textile manufacturing, sizing agents, mineral oils or acrylate-based spin finishes are applied, which form a film around the yarn or individual fibers to reduce friction and electrostatic charging. Due to the interaction of reactive plasma species, textile surfaces can be etched physically and chemically. Ion bombardment, radical density and VUV (vacuum ultraviolet) radiation determine the etching rate depending on reactor geometry, plasma excitation, gas type, flow, power, pressure and textile material (Liston, 1993). Typical etch rates of organic materials are a few nanometres per second. Therefore, a plasma treatment can be used for the cleaning of manufacturing residuals on textiles. Plasma cleaning is a prerequisite to obtaining good adhesion, e.g. to a subsequent plasma coating, and can be performed in a one-step process.

6.4.1 Fabrics

Analysis of an industrially washed PET fabric by XPS revealed an enhanced hydrocarbon (C—C, C—H) peak at 284.6 eV compared with a PET



6.3 XPS spectra of (a) PET reference spectrum, (b) PET textile fabric as received (industrially washed), and (c) plasma-cleaned PET textile fabric.

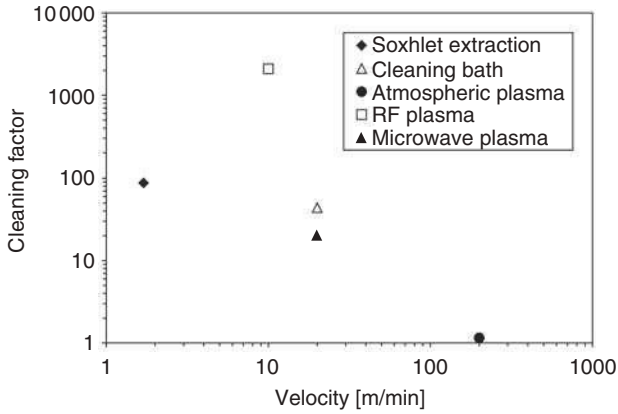
reference spectrum (Figure 6.3). Using Soxhlet extraction, the weight of the residuals can be determined and the corresponding thickness can be calculated. For the as-received textile fabric (industrially washed), a residual layer of 3–4 nm was found, which might be inhomogeneously distributed. This result agrees well with the XPS obtained depth of ~5 nm.

A short plasma treatment using a gas mixture of argon and oxygen (RF plasma, 10 m/min, 0.2 W/cm^2, 20 Pa) totally removes the residual spin finish and leads to an additional activation of the polymer, indicated by new functional groups around 287.2 eV as shown in Figure 6.3 (Hossain, 2006a). While argon causes mainly physical degradation by chain scissions, whereby also redeposition occurs, atomic oxygen produced in the discharge (by energy transfer and VUV light activation through the inert gas) results in chemical etching and the formation of volatile compounds such as CO_2 and H_2O. Hence, a complete cleaning can be obtained by a plasma treatment. However, the plasma cleaning should be adapted to the textile structure of the treated fabric (Hossain, 2006b).

Moreover, a plasma treatment with non-polymer forming gases might be used prior to the grafting of monomers onto fabrics or after the soaking of fabrics within a monomer solution to induce cross-linking (Castelvetro, 2006). Conventional wet-chemical treatments such as pad dyeing with fluorocarbons can also be improved after plasma cleaning and activation to achieve excellent stain repellencies (Hegemann, 2005c).

6.4.2 Fibres

On commercially available, continuous multifilament yarn made of polyester, 4.4 wt% of oily substances were found, which corresponds to an about 180 nm thick contaminant layer (Keller, 2005). A comparison of different cleaning methods on these polyester fibres proved RF plasma cleaning (Ar/O_2 or He/O_2, 10 m/min, ~0.2 W/cm^2, 100 to 700 Pa) to be ideal (Figure 6.4). The velocity can be enhanced by leading the fibres several times through the plasma zone. Moreover, the lowest amount of waste resulted



6.4 Effectiveness and efficiency of different cleaning methods in terms of cleaning factor vs. velocity. The cleaning factor is defined as the ratio of initial to residual contaminants on the PET yarn. A factor exceeding 1000 can be considered as complete removal of the mineral oils.

from the plasma cleaning, demonstrating its potential as an eco-friendly technology.

6.4.3 Scale-up

Plasma cleaning is controlled by energetic particles (physics) and radicals (chemistry). The transfer of plasma activation and etching processes with non-polymerisable gases between various reactors was found to depend on the energy flux to the substrate, which is mainly determined by the sheath voltage, the pressure (by collisions within the plasma sheath) and the plasma power density (power per area) controlling the ionisation degree (Kersten, 2001). Thus, the scale-up of plasma cleaning can easily be achieved by maintaining gas composition and pressure and adjusting the power input regarding the area of the treatment (W/cm^2).

6.5 Plasma metallisation

For the metallisation of textiles, sputter-based processes can be effectively used. Sputtering can be characterised as a non-equilibrium process at the energy range of interest for film deposition (Rossnagel, 2003). Sputtering is initiated by the impact of energetic particles (in the order of 100 eV) on a target material, e.g. a metal. The incident particle causes a multiatom kinetic collision process, whereby atoms near the surface may be dislodged with enough energy to overcome the surface binding energy and be emitted from the target. These atoms are known as sputtered atoms, and when they

deposit on some other surface, the process is called sputter deposition. Inert gases such as argon are generally used for the sputtering of metals, whereas an addition of reactive gases (O_2, N_2 etc.) yield reactive sputtering and, e.g. metal oxides or nitrides. Moreover, alloys, ceramics, and polymers can be used as target materials. The energy of the incident particles can be enhanced by electrical and magnetic fields, while avoiding collisions. Therefore, we are mainly using magnetron sputtering with argon at a pressure of 1 Pa to obtain metallisations on textiles and fibres.

6.5.1 Fabrics

Fabrics made of mono- or multifilamentary fibres or yarn show uncovered and covered areas at superposed fibres/filaments. Since sputtering is mainly a directed deposition due to high sticking coefficients of the atom/cluster flux from the target to the substrate, an inhomogeneous film growth on structured surfaces such as fabrics can be expected. To investigate this effect, we deposited copper coatings on tightly woven PET fabrics using DC magnetron sputtering. The substrates were fixed on the rotating drum of our web coater. Treatment times of 15, 30 and 60 min were used at an argon pressure of 1.5 Pa to obtain around 100, 200 and 400 nm thick Cu films, respectively (measured on Si wafers). The surface resistivity on the fabrics was measured according to EN1149-1. The short deposition time of 15 min results in a high resistivity of $10^{13}\,\Omega$, whereas $6*10^{10}\,\Omega$ was obtained for 30 min and $10^{10}\,\Omega$ for 60 min of sputtering time. Note that the surface resistivity – though the current is restricted to a thin surface layer – is still dependent on film thickness for nano-scaled coatings on textiles. Hence, the lowest film thickness or disconnected areas along the coated fibres of the fabric, which might be found at superposed fibres (thus also depending on the textile structure), determine the conductivity of a metallised fabric. For an anti-static treatment of fabrics, a surface resistivity below $5*10^{10}\,\Omega$ is needed. Depositions of more than 200 nm are thus required to obtain anti-static fabrics by magnetron sputtering due to the inhomogeneous coating. However, thicker coatings show some crack formation detected by scanning electron microscopy. The direct metallisation on fibres is thus of high interest for the deposition of more homogeneous, nano-scaled coatings to achieve a good conductivity by maintaining the textile properties.

6.5.2 Fibres

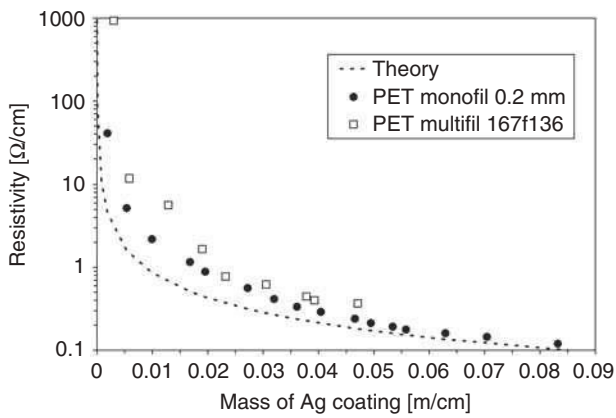
Magnetron sputtering of metals on fibres, which can be performed using our fibre coater, provide conductive/anti-static and in the case of silver also anti-bacterial surfaces (Amberg, 2004). After a cleaning step as described in Section 6.4.2, the fibres are metallised in a continuous process by moving

them several times through the plasma zone created inside the cylindrical magnetron. Thus, a homogeneous, all-side coating can be achieved. When the fibres are moved back to air, the electrical resistivity is measured on-line. By variation of the plasma conditions (power: 200 to 4200 W; pressure: 1 to 5 Pa) and the process velocity (0.3 to 80 m/min), the amount of the sputter-deposited metal, i.e. the deposited mass or the coating thickness, can be controlled. If a homogeneous coating without defects is assumed, the resistivity per length of the fibre (in Ω/cm) can be calculated from the deposited mass of the metal per length of the fibre m/l (in g/cm) by

$$\frac{R}{l} = \rho_{el}\rho\left(\frac{m}{l}\right)^{-1} \qquad [6.1]$$

with the specific electrical resistivity ρ_{el} (in Ω/cm) of the considered metal and its density ρ (in g/cm^3). These theoretical values were compared with real coatings on PET monofilament fibres (∅ 0.2 mm) and PET yarn (167 f144) for different amounts of sputter-deposited silver (Figure 6.5). Note that the deposited mass was used as parameter, since it can be measured more precisely compared to, e.g. the coating thickness. The obtained resistivity was averaged over several metres of coated fibre. Untreated PET fibres showed a resistivity of around 10^{11} Ω/cm.

It can be seen that, for lower amounts of deposited silver, the measured resistivity was higher compared to the calculated values for ideal coatings, but approached the theory for thicker coatings. Effects such as oxidation at the surface, interface formation between polymer fibre and metal, as well as inhomogeneous coating thickness, are responsible for this finding. In



6.5 Measurement of the resistivity on Ag-coated polyester mono- and multifilament fibres and comparison with theoretically expected values for ideal coatings.

particular for the yarn, some inner filaments were covered and the electric current was mainly conducted by the outer filaments resulting in 'bottle necks' for nano-scaled coatings (<50 nm). Therefore, a coating thickness of around 100 nm is required to obtain a resisitivity of 1 Ω/cm, which is appropriate for good conducting fibres. These Ag-coated fibres are suitable for the development of flexible electrical connections in *smart textiles* and for *wearable computing*. Nano-scaled coatings, however, are adequate to obtain anti-static effects that may be required for medicinal or occupational textiles and electrostatic shielding.

Since thinner coatings can be applied using magnetron sputtering in comparison with electrochemical silver coatings, lower amounts of metal are needed and the textile properties of the fibres remain unaffected. These fibres can thus be processed in a similar manner to uncoated polyester fibres, i.e. Ag-coated textile fabrics can be woven or single Ag-coated fibres can be integrated into a textile fabric with defined spacing. Moreover, in contact with the human skin, silver ions are released from the ultrathin coatings, which reveal a strong anti-bacterial and fungicidal effect.

6.5.3 Scale-up

Due to the low pressures used (<5 Pa), the sputtering of a target material is controlled by the energy and the number of bombarding particles, which gives the corresponding sputtering yield. The process transfer of sputtering with inert gases thus depends on the energy flux to the target, which is mainly determined by electrical and magnetic fields and the plasma power density (power per area) controlling the ionisation degree, while the plasma sheath can be considered as collision-free. Moreover, the geometry of the reactor has to be considered, since the number of collisions between sputtered atoms and the background gas is given by the pressure p and the distance between target and substrate d. Thus, the scale-up of sputtering can be achieved in a first approach by maintaining the number of collisions ($p*d$) and adjusting the power input regarding the area of the treatment (W/cm^2).

6.6 Plasma polymerisation

Plasma polymerisation on textiles has gained increasing interest during the last decade, since highly functional surfaces are enabled, resulting in several industrial applications (Hegemann, 2006a). High-value added products with new functionalities such as water/stain repellence, permanent hydrophilicity, dyeability, abrasion resistance, and biocompatibility can be generated due to the nano-scaled modification of fabrics and fibres. At the same time, the bulk properties of the textiles remain unaffected. Moreover, due to the

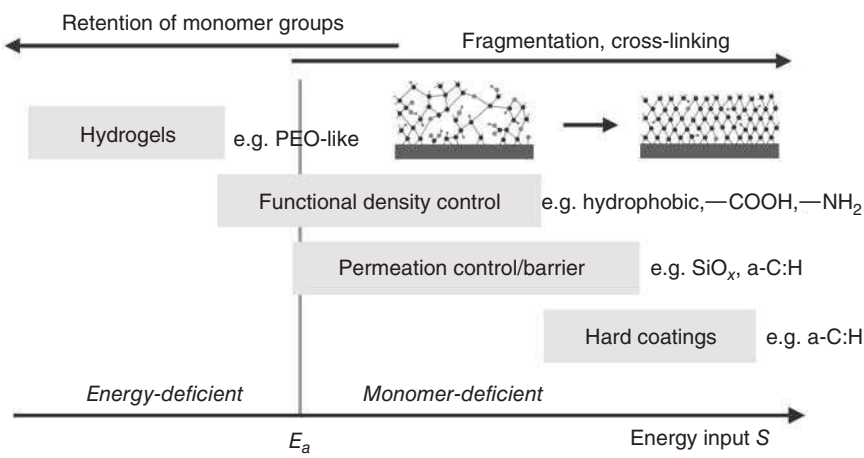
replacement of wet-chemical processes and a low material and energy input, plasma polymerisation provides the realisation of environmentally sound processes.

Plasma polymerisation, which means radical-promoted processes, can be described by the composite parameter power input per gas flow W/F, which relies on the concept of macroscopic kinetics (Rutscher, 1993; Yasuda, 2005). This statistical approach considers the energy invested per particle within the active plasma zone yielding an excited state, such as a radical, and subsequent recombination in a passive zone, yielding a stable product such as a deposition. Hence, the expansion of the plasma has to be taken into account (Hegemann, 2006b). A monomer-dependent activation energy E_a can be derived by evaluating the mass deposition rates R_m (Hegemann, 2001; Hegemann, 2005a) considering that

$$\frac{R_m}{F} = G\exp\left(-\frac{E_a}{W/F}\right) \qquad [6.2]$$

with a reactor-dependent geometrical factor G. An Arrhenius-type plot of Equation [6.2] by variation of W/F parameters gives a straight line, where its slope corresponds to E_a, proving the validity of this approach. Deviations might be found at low and high energies due to oligomers taking part in film growth and energetic particle interactions, respectively (Hegemann, 2005b).

At an energy input below the activation energy, for example, swellable hydrogel films can be deposited such as polyethylene oxide-like coatings (Figure 6.6). By increasing the energy input into the active plasma zone, the



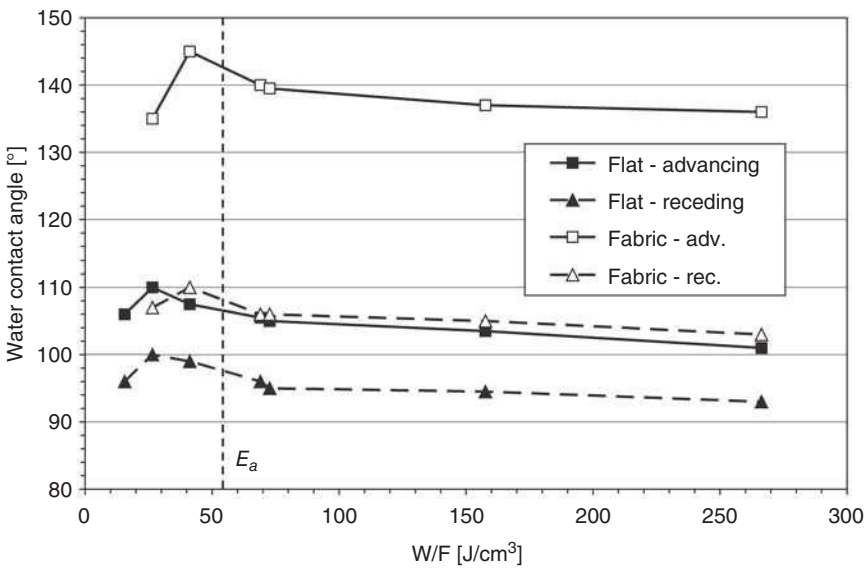
6.6 Different regimes of functionality and cross-linking that can be covered by plasma polymerisation depending on the energy input.

degree of retention of functional groups can be controlled due to enhanced fragmentation at higher energies. Further increase of energy input leads to the formation of dense barrier coatings, when, e.g. hydrocarbons are used as precursors.

6.6.1 Fabrics

Different (low-pressure) plasma polymerisation processes applied to textile fabrics have already been transferred to an industrial level (Hegemann, 2006a). Siloxane coatings derived from organosilicone discharges are used as durable, fluorine-free hydrophobic coatings. Plasma polymers consisting of a Si—O backbone with retained methyl (CH_3) groups yielding low surface energies can be achieved, e.g. by using hexamethyldisiloxane (HMDSO) as monomer. While the hydrophobic properties of pp-HMDSO coatings slightly decrease at increasing energy input, the cross-linking and thus the mechanical properties, can be enhanced (Hegemann, 2001). As shown in Figure 6.7, remarkably higher contact angles can be achieved with structured textile fabrics compared to flat surfaces such as PET foils (Hegemann, 2005d).

The addition of oxygen to HMDSO discharges enables the reduction of hydrocarbon incorporation during film growth, increasing the inorganic



6.7 Plasma polymerised HMDSO coatings used for the hydrophobization of PET fabrics. Due to the textile structure, higher contact angles can be achieved compared with flat surfaces.

character of the coatings and further enhancing the mechanical properties. Thus, abrasion resistant, quartz-like coatings can be deposited on flexible materials when a gradient layer is applied to reduce internal stresses at the interface polymer/coating (Hegemann, 2005a).

Fluorocarbons, on the other hand, are plasma polymerised as stain repellent coatings, showing better durability compared to common wet-chemical treatments (Zhang, 2003). Moreover, textile properties such as feel (touch), optics, and mechanical strength remain unaffected by the nano-scaled plasma polymers covalently bonded to the textile surfaces.

Diamond-like carbon (DLC) coatings deposited on fabrics within hydrocarbon plasmas were investigated for their mechanical, tribological and biological properties (Hauert, 2003). Adhesion on flexible substrates could be enhanced by interfacial gradient layers.

The key factor for plasma polymerisation, however, is given by the add-on value outperforming other available techniques. Examples are tailored plasma polymers containing functional groups to achieve permanent hydrophilic treatments for improved wicking, adhesion and dyeability (Hegemann, 2006a; Hossain, 2006c) or specific binding of linker molecules enabling regioselective treatments on hollow fibres used for blood dialysis (Oehr, 2005).

6.6.2 Fibres

Siloxane coatings using a HMDSO discharge can also be deposited directly on fibres, in a continuous process, to obtain, for example, a hydrophobic, water-repellent yarn. A PET yarn (167 f136) was conducted several times through the deposition chamber of our fibre coater to increase the velocity of the plasma polymerisation process by parallel treatment. An RF antenna was used to activate the glow discharge placed at the centre of the cylindrical vacuum chamber, in parallel to the aligned yarn sections. Regarding the continuous process, each section of the yarn passes different zones of the plasma chamber by moving along the axis and through different radial positions due to the directional change of the yarn. Since the deposition is performed on floating potential to obtain an all-side treatment of the fibres, the deposition rate depends on the luminosity distribution and thus the plasma density of the unconfined plasma around the RF antenna, which was found to decrease with the distance to the antenna after passing a maximum at the plasma/sheath boundary. Thus, varying deposition conditions should be regarded for a continuous plasma polymerisation on fibres. However, we found that the film chemistry (retention of methyl groups and cross-linking) using a HMDSO discharge mainly depends on the energy input by the reaction parameter W/F which is also influenced by pressure, yielding a broader active plasma zone at lower pressures and less on the

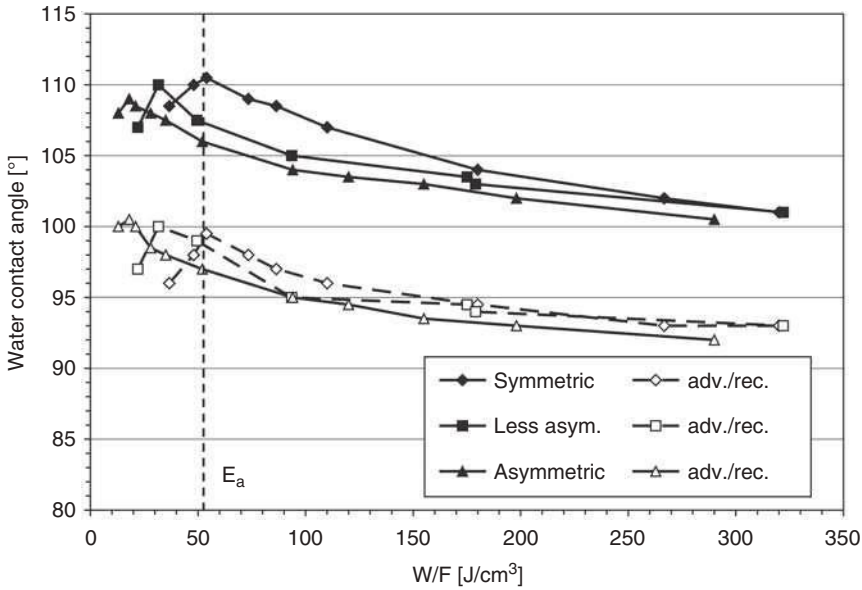
deposition position within the plasma chamber. Hence, almost constant deposition conditions with respect to film chemistry can be obtained by using a suitable feed-in of the HMDSO monomer. Nano-scaled functional plasma polymers can thus be deposited directly on the fibre geometry within a continuously running process.

6.6.3 Scale-up

The retention of functional groups and the degree of cross-linking of plasma-polymerised films is determined by the absorbed energy (J/cm^3) within the active plasma zone and the interaction of energetic particles during film growth (given by the sheath potential and pressure). Using RF plasma excitation, which enables well-defined deposition conditions with respect to the plasma expansion and power coupling, the influence of energetic particles can be enhanced by reducing the pressure (less collisions within the plasma sheath) or increasing the degree of asymmetry, since smaller RF electrode areas cause higher bias potentials. Therefore, we compared different reactor geometries by performing HMDSO discharges. Regarding the real power absorbed within the active plasma zone (by considering the plasma expansion) and the real flow contributing to film deposition (by considering by-passing of flow) we were recently able to prove that the activation energy of plasma polymerisation derived from mass deposition rates following Equation [6.2], i.e. the plasma chemistry solely depends on the reaction parameter W/F, which can be used for the scale-up (Hegemann, 2005e). For symmetric reactors, the highest recorded water contact angles, which result from the retention of methyl groups during deposition, coincide with the obtained activation energy for HMDSO discharges (Hegemann, 2001). For asymmetric reactors, however, a shift towards lower energy inputs was obtained (Figure 6.8), indicating the increasing influence of energetic particle bombardment. Further increase of the particle bombardment, which can be controlled by the bias potential, leads to rivalling deposition/etching conditions, and the approach of macroscopic kinetics regarding the specific energy W/F fails. After a transition region (above a bias voltage of about 100 V), however, the properties of amorphous hydrocarbon (a-C:H) coatings, for example, can be controlled by the bias potential, which can be used for the up-scaling of DLC coatings (Jacobsohn, 2002; Rangel, 2004).

6.7 Plasma co-polymerisation

Although the field of medical devices has made significant technological advancement, the bacterial colonisation of biomaterials remains a major clinical problem, often leading to device failure, and can be fatal (Vincent,



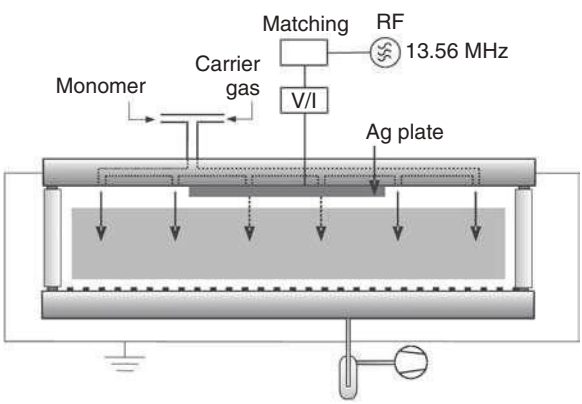
6.8 Advancing and receding water contact angle of plasma-polymerised HMDSO coatings, depending on the energy input and the degree of asymmetry of the RF plasma set-up.

1995). Although the precise mechanism of infection has not been identified, it is well known that the surface properties of biomaterials (e.g. chemistry, wettability and morphology) play an important role in their interaction with the surrounding environment and the success of their application (An, 1998). One of the more effective anti-bacterial methods currently under investigation is based on the design of a coating that contains silver (Balazs, 2004a, 2005a; Davies, 1997; Fox, 1969). The toxic effects of metallic and monovalent silver are bacterial-specific and contact will prove fatal to pathogens containing sulfhydryl functional groups (Davies, 1997). Silver has been proven effective in killing over 650 disease-causing organisms, and is active against gram-negative bacteria, such as *Pseudomonas aeruginosa*, as well as gram-positive bacteria, fungi, protozoa and certain viruses. The 2500-year history of application in water purification has further established the non-toxicity of silver at low concentrations, and Davies and Etris (1997) further describe that monovalent silver is non-toxic to mammalian cells because sulfhydryl (—SH) groups are not exposed on the membranes. However, the cyto-toxicity of Ag is still under scrutiny for certain medical applications (Stickler, 1999). Due to the bacterial-toxic effects of released silver ions (Davies, 1997), it is hypothesised that Ag/plasma polymer films may offer long-term resistance to bacterial adhesion and prevent the colonisation of biomaterial surfaces. Such Ag/plasma polymer nano-composite

materials, consisting of nano-scaled metal clusters embedded within a plasma–polymer matrix, can be deposited using a mixed plasma polymerisation/sputtering process (Favia, 2000; Balazs, 2005a). For example, Ag containing plasma polymer nano-composites are deposited employing a silver cathode, an appropriate monomer to yield the desired material properties of the matrix (non-fouling, cell-adhesive, hydrophilicty, etc.) and an asymmetric reactor design, as illustrated in Figure 6.9.

The plasma deposition of nano-Ag/plasma polymer films can be described as a mixed process, including the deposition of a plasma polymer matrix and the sputtering of silver atoms; the sputtering of silver necessitates that the discharge is operated at conditions that favour ion bombardment of the cathode, including lower pressure (*ca.* 0.1 mbar) and higher input power than is commonly used for plasma polymerisation. Unfortunately, such conditions also correspond to a high monomer fragmentation regime, and can result in a decreased functionality of the plasma polymer matrix. Therefore, the deposition of nano-Ag/plasma polymer films can be considered as a compromise between having an acceptable quantity of silver to add an anti-bacterial property, and maintaining enough of the functionality of the matrix in order to confer additional properties of the coatings (Balazs, 2005a). Nano-particle quantity and matrix characteristics of the films can be tailored to specific requirements by altering deposition parameters such as power input, pressure and Ar feed ratio (Balazs, 2005a, b).

Examples of such coatings include Ag/ poly(ethylene-oxide) (PEO)-like (Ag/PEO-like) coatings, which combine the non-fouling properties of conventional PEO materials that hinder the adsorption of proteins and the germicidal properties of silver ions released in media which occurs upon swelling of the hydrogel matrix. Retention of the ether carbon functional-

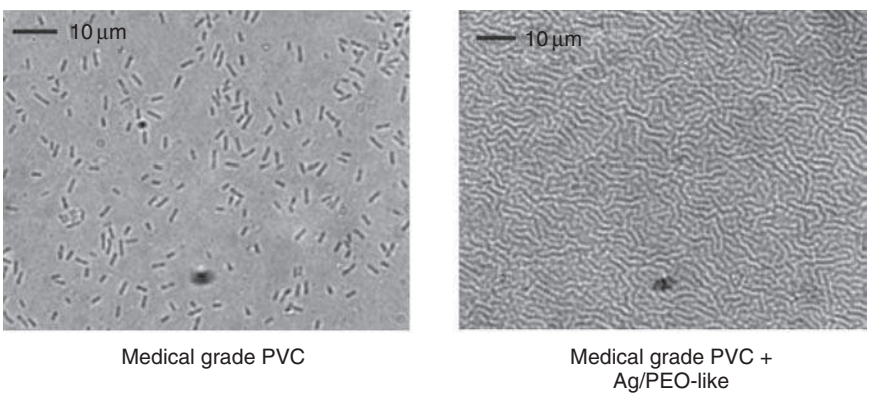


6.9 Schematic representation of the asymmetric plasma reactor used to deposit Ag/plasma polymer nano-composites.

ities in the monomer, often referred to as the 'PEO-character', has been demonstrated to be the determining factor of the non-fouling nature of plasma-deposited PEO-like coatings (Lopez, 1992; Favia, 1998). Despite their reduced PEO character as compared to films produced under low monomer fragmentation conditions, Ag/PEO-like coatings completely prevented the adhesion of four different *P. aeruginosa* strains when deposited on medical grade PVC. The 100% reduction for the PAO1 *P. aeruginosa* strain following Ag/PEO-like coating deposition on PVC is illustrated in Figure 6.10 (Balazs, 2005a). Another example includes Ag/Teflon-like coatings which were also capable of reducing adhesion of a 1.1A1 *P. aeruginosa* strain by 86% and 93% as compared to medical grade PVC and Ag-free Teflon-like thin films (Balazs, 2004b, 2005b). It was demonstrated that increasing the Ag-content, through changes in input power, allowed for an increased reduction in bacterial adhesion.

By changing the target material used at the cathode, this technique also allows for the possibility to include various metallic or ceramic nano-clusters. In addition to silver, some other examples of a nano-composite used in biotechnology are Au-containing Teflon-like (d'Agostino, 1991) and quartz-like coatings (Fracassi, 1996), where the released Au nano-particles were found to specifically bind to cancer cells (El-Sayed, 2005). Ceramic TiO_2 nano-particles might be also of interest as UV-absorbing layer for synthetic fibres, or odor repellent textiles (Wedler, 1999).

In addition to all of the advantages of plasma processing techniques, the formation of metal nano-cluster/plasma polymers by this technique allows for an *in situ* immobilisation of nano-particles that is possible during plasma deposition, providing a one-step coating process that eliminates the



6.10 Micrographs illustrating the bacterial adhesion of the PAO1 *P. aeruginosa* strain to medical grade PVC (left) and Ag/PEO-like coatings (right).

necessity of direct handling of nano-particles (Balazs, 2005a; Favia, 2000). Furthermore, through the incorporation of nano-particles in a polymer matrix, it is possible to significantly reduce the amount of metallic material as compared to electrochemical techniques, thus having an important effect on cost, especially when precious metals, such as silver or gold, are considered. This technique allows the possibility to control how much metallic material is incorporated in a coating through changes in particle size.

6.8 Future trends

Low-pressure plasma processes have made inroads even where economic margins are slim, since plasma treatments have unique capabilities and are environmentally benign. Thus, many conventional processes, mainly wet-chemical ones, can be replaced.

The approach to deposit nano-scaled coatings on textiles is of special interest, since textile bulk properties remain unaffected. For example, metallised fibres can be woven under the same conditions as untreated fibres or yarn. Integrating electronics into clothing is an important new concept, which opens up a whole array of multi-functional, wearable electro-textiles for sensing/monitoring body functions, delivering communication facilities, data transfer, individual environment control, and many other applications (Tao, 2005).

Controlled drug delivery is an important development in biotechnology, where plasma processing allows for the production of novel substrates with tight control of polymer cross-linking and release rates upon swelling. The production of multi-layer, gradient and reservoir systems which are difficult to achieve by wet chemical techniques are greatly facilitated by plasma processing. Smart textiles that enhance wound healing, prevent infection or provide feedback to physiological responses will be important product developments for human well-being.

Hydrophobic and oleophobic coatings are still of high interest, since wet-chemical treatments reveal a lack of sufficient washing fastness. Thus, cross-linked plasma coatings should further be examined. The same holds for permanent hydrophilic coatings, where new types of nano-scaled functional plasma coatings that show reduced ageing and enhanced washing fastness are currently under investigation.

Hence, textile trends that are relevant for plasma treatments deal mainly with hydrophobic/oleophobic, hydrophilic functional, anti-static and conductive, anti-microbial and medicinal coatings, as well as multi-functional surfaces. A further trend will lead to strong, thermally stable and highly abrasion-resistant textiles, where plasma technology will also have a contribution. Besides functionality, the comfort of functional textiles for the user becomes more and more a main focus.

6.9 Sources of further information

Wearable Electronics and Photonics (Woodhead Publishing, 2005) edited by X. M. Tao (Hong Kong Polytechnic University) shows the major new concepts of integrating electronics into clothing and explores future trends for fashion and specialist clothing. Surface properties of textiles, which are relevant for plasma treatments, are covered by C.M. Pastor and P. Kiekens *Surface Characteristics of Fibers and Textiles* (Marcel Dekker, 2001). A comprehensive overview of sputter deposition is given by W. Westwood in *Sputter Deposition* (AVS Education Committee Book Series, Vol. 2, 2003). Plasma polymerisation is extensively treated by H. Yasuda in his new book *Luminous Chemical Vapor Deposition and Interface Engineering* (Marcel Dekker, 2005). Industrial-size plasma reactors are delivered, for example, by Europlasma (www.europlasma.be) or Sigma Technologies International (www.sigmalabs.com). Know-how in continuous plasma deposition and reactor development can further be used, e.g. from Plasma Finish (plasma polymerisation; www.plasma-finish.com), Von Ardenne Anlagentechnik (sputtering; www.vaat.biz) and Roth & Rau (fibre coating; www.roth-rau.de).

Empa's activities within its Department 'Materials and Systems for Protection and Wellbeing of the Human Body' can be looked up at www.empa.ch.

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