

Part II

Textile applications

7.1 Introduction

Most liquid-repellent textile treatments are simply treatments exclusively for textiles and are often specific to individual textiles. It would be a great advantage if the same levels of liquid repellency could be applied to a multitude of textiles and materials, independent of composition, with the added benefit of being able to apply it to the final product. Plasma technology allows this to be realised, where one of the main features is the ability to place the entire end product into the chamber and render all components liquid repellent, i.e. not just the textile or material but the zips, seams and fasteners, protecting the whole item from liquids. This benefit extends into all market areas, where the end product can undergo the plasma enhancement process to provide the liquid-repellent properties.

Many chosen materials in products all around us are selected either for their bulk physical properties or ease of processing. However, their resulting surface properties can be far from ideal for their intended use. Plasma processing allows the surface properties, typically from angstroms (10^{-10} m) to 10s–100s of nanometres (10^{-9} m) in thickness, to be further optimised, without affecting the bulk properties, and allowing the product to perform at a much higher level in its intended application and often opening up new applications altogether. It is desirable to offer high levels of water and oil repellency, especially for adverse weather conditions and proximity of textiles to liquids, such as food and beverages that can easily come into contact with items of clothing and furnishings.

This chapter considers the requirement for water and oil repellency for textiles and looks at the features and benefits, along with the critical factors of a diverse number of products in a number of industry sectors (Section 7.2). The theory and testing of water and oil repellency is explained in Section 7.3 with current solutions for rendering textiles water and oil repellent being covered in Section 7.4. The use of plasmas for imparting liquid repellency is addressed by a case study of the scale-up issues faced with

commercialising a low-pressure plasma process for imparting water and oil repellency (Section 7.5), which also touches on some of the background work on the use of plasmas to achieve this technical effect. Finally Section 7.6 covers what the future holds and outlines a vision for plasma processing and important milestones that need to be achieved for the technology to be commercially acceptable. A list of useful references where further information can be sought, in addition to the details of where much of the information has been sourced, is cited in Section 7.7.

7.2 Requirement for water and oil repellency

7.2.1 Providing added value

Customers demand increasing functionality from products they buy. Examples include something as complicated as greater resolution on medical instrumentation, as demanding as temperature tolerances of solar panels on space shuttles, or simply a longer lasting filter for their car or a suit that does not get wet when it rains. People either want more for their money or are willing to pay for the benefits of a differentiated product. Either way, if a company wants to become successful by delivering a more cost-effective solution or increasing market share, it must innovate and provide value-added solutions. This value-added feature can be far ranging, from a tangible differentiator such as a new colour or technical effect, to a less tangible factor such as use of an environmentally friendly process. This section will concentrate on the tangible benefits of added technical effects.

All products around us have several things in common:

- They are generally made of more than one material, such as plastics, textiles, glass, ceramics, metals, rubbers, wood
- They require the assembly of smaller components or raw materials in order to become a usable product
- They will come into contact with different environments throughout their life-time, such as various liquids, temperatures and abrasive conditions and
- The performance properties required of the product may be very different from those of the raw materials selected to make the components of the product.

To expand on the last point, materials will be chosen for many different factors, such as cost, ease of processing, historical reasons or performance requirements. In most cases, the materials chosen will not only give rise to the bulk properties but also the surface properties, and for many products it is the interaction with the surface that either dictates the performance or

is a very effective way of adding considerable value through a differentiating technical effect. For many devices, an optimum solution would be to process using cheap, well-known, manufacturing-friendly materials and then modify the surface using an additional process to impart whatever functionality is required.

Many added-value technical effects are available, such as flame retardancy, antimicrobial properties, ability to conduct electricity or thermal energy, anti-corrosion, anti-smear, anti-fogging, protein resistance, hydrophilicity, haema compatibility, oil and water repellency; and this is far from an exhaustive list. Many of these properties are already available; however, it may only be possible to apply them to a small number of materials due to limitations with processing techniques. What the majority do have in common is a durable surface application that is product specific. It is often not necessary to apply the technical effect throughout the bulk of the materials used to make up that product. This presents interesting opportunities for adding value to textiles using a universal surface modification technique.

7.2.2 Focus on water and oil repellency

Liquid repellency is a wide-reaching technical effect that is sought after in several industry sectors, from biosciences, healthcare and electronics to industrial filtration, sports and active wear. Often, repellency to water alone is not enough and other liquids such as oils, inks and alcohols need to be repelled. Liquids are constantly in use around us, in the majority of cases in the form of rain water and food and beverages. Arguably, the most noticeable, unfavourable interactions of these are with textile products such as clothing, carpets and upholstery, so added value can be provided by simply protecting these items from interacting with the liquids, enabling the liquids to roll off or be dabbed away, leaving the underlying material unchanged. The theory behind this will be covered in detail in Section 7.3.

Providing liquid repellency to textiles has always been a desirable effect as very few are inherently liquid repellent and the variety of substrates possible has led to many different methods of applying the technical effect; this will be covered in some detail in Section 7.4. By breaking down the different industry sectors into products, features and benefits of liquid repellent properties, an idea of why liquid repellency is so far reaching for textile applications can be illustrated (Table 7.1). Examples of some of the required critical factors are also included in the table.

Although more simply termed water and oil repellency, the description covers repellency of many other liquids including inks and alcohols. Further challenges are presented when more viscous liquids or solid/liquid slurries containing reactive dyes and acids come into contact with a material, due

Table 7.1 Breakdown, by industry sector, of product benefits and critical factors of liquid repellent treatments of textiles

| Industry sector | Example products | Features/Benefits | Critical factors |
|--------------------------|---|--|---|
| Medical | <ul style="list-style-type: none"> Bandages | <ul style="list-style-type: none"> Prevents both water ingress and blood/ointment wicking Less pain for patient or chance of rupture when detaching from wound | <ul style="list-style-type: none"> No cytotoxicity or leachables |
| Electronics | <ul style="list-style-type: none"> Fuel cells | <ul style="list-style-type: none"> Reduces liquid transport Increases battery lifetime Ability to harbour more power | <ul style="list-style-type: none"> Provide robust effect that is not easily broken down |
| Automotive and aerospace | <ul style="list-style-type: none"> Seat covers | <ul style="list-style-type: none"> Minimises staining – fresh look for longer Minimises odour and smoke uptake – improved hygiene Easy clean | <ul style="list-style-type: none"> Durability for product life-time Product often a complex 3D shape Can it be re-processed? |
| Fashion | <ul style="list-style-type: none"> Designer shoes, bags and clothing | <ul style="list-style-type: none"> Retains desired look and colours for longer, as often not possible to clean due to material or design selection | <ul style="list-style-type: none"> Must not impair aesthetics or hand; no perceivable change is acceptable |
| Sports and active wear | <ul style="list-style-type: none"> Trainers Lightweight jackets | <ul style="list-style-type: none"> Waterproof performance with minimal heat stress Rain protection in lightweight garments Wearer stays dry and garment remains light | <ul style="list-style-type: none"> Maximised performance for product life-time Wash durability |
| Military | <ul style="list-style-type: none"> Military warfare clothing | <ul style="list-style-type: none"> Resists chemical agent challenges such as nerve agents and mustard gas, in addition to environmental challenges such as rain water | <ul style="list-style-type: none"> Very low surface energies required Often need to include many different technical effects into as few a layers as possible Durability requirements need to be met |

to the rheology or reactive nature. It is not the intention to discuss this in detail, as they are covered in great depth in other texts, but to concentrate more on the general requirements of repellency.

7.3 Theory and testing of water and oil repellency

7.3.1 Surface energy and surface tension

The science of liquid repellency is often overlooked. Generally speaking, the phenomenon relies on three main aspects:

- surface energy of the base material
- surface energy of the coated material
- surface tension of the liquid in contact with the surface.

Although there are other contributing factors, just the interactions of solids with liquids will be addressed for the purpose of this discussion.

Repellency in itself is a confusing term as this is often perceived as forcing something away, in the way that like magnetic poles repel each other. The majority of liquid repellents do not 'force' the liquid away, but merely present an inert surface where fewer interactions take place. Having said this, the term repellency will be used to describe this phenomenon due to its popular acceptance.

All solid surfaces have surface energy, which is a function of surface area and the amount of electronic charge present, made up by the molecules at that surface. In addition, all liquids have a surface tension, which is a measure of the interaction energies between the molecules that make up that liquid when at the gas/liquid interface. The most common units used to measure surface energy and surface tension are dynes/cm and mN/m, i.e. force per unit length which is analogous to energy per unit area.

Liquids such as water have a high surface tension due to the strong interactions between the polar water molecules. At the air/water interface, this interaction energy is exhibited by the surface molecules displaying a 'skin' like effect. Oils have low surface tensions as there are only very weak interactions between the apolar molecules.

All liquids, as is common with many things in nature, wish to attain the minimum energy state possible and are mobile enough to do that. They will move to minimise the interfacial tension between themselves and the environment they are in. What this means in practice is that, for a pure liquid suspended in mid air, providing there are no external forces, the shape adopted to minimise the interfacial tension is that of a sphere, i.e. the geometric shape where the maximum number of molecules are in contact with each other. As external energy is provided, such as a surface, the shape will adjust to minimise the new interfacial energy.

Water has one of the highest surface tensions of common liquids around us, with a value of ~ 72 mN/m at 20°C . It should be noted here that surface tension and surface energy are a function of temperature, and they will increase as temperature increases. Generally speaking, high surface tension liquids will sit with high contact angles on a low surface energy material; for example, a droplet of water on a freshly waxed car. Conversely, low surface tension liquids will sit with low contact angles on high surface energy materials, for example, olive oil in a metal frying pan.

In reality, few surfaces are truly flat, and especially so in the textile world. It is important to understand how the surface roughness affects the interactions between the liquid and the material contacting and this will help explain why textiles are adversely affected by liquids.

7.3.2 Surface roughness

Surface roughness will enhance the repellency effects seen on a flat surface of the same chemical composition. Generally speaking, and taking water as an example, if a droplet of water is in contact with a flat material and has a contact angle greater than 90° , then if the surface is roughened, the contact angle will increase, displaying super hydrophobicity. The material is said to be inherently hydrophobic and less energy is required to move the droplet across the surface (Figure 7.1). Conversely, if the droplet of water is less than 90° on a surface, then the material is inherently hydrophilic, and roughening the surface will result in a lower contact angle, as greater interaction energy results (Figure 7.2).

7.3.3 Achieving liquid repellency

As described earlier, many materials do not display the surface properties required for a particular product to function as required and there is a need



7.1 Super hydrophobicity resulting from surface roughening of a hydrophobic surface.



7.2 Effect of surface roughening of a hydrophilic surface.

to change these properties in order to give the product a much wider scope of use. Very few textiles are inherently water repellent and none are oil repellent. Therefore, an additional process must be added to display these properties. This process can be any one of a number of techniques which will be discussed in greater detail in Section 7.4. All the techniques apply lower surface energy chemical groups to the surface in order to reduce the interaction energies. The main three chemicals used to deliver these groups are hydrocarbons, silicones and fluorocarbons, which can be used alone or in combination.

Hydrocarbon and silicone based repellents only repel water, so if oil repellency is required, fluorocarbons have to be used to some degree. Fluorocarbons are far more expensive than hydrocarbons, especially when used in large quantities, which is why they are often co-applied. Finding techniques for reducing the amount of fluorocarbon used, whilst still retaining the high levels of repellency, are much sought after.

Fluorocarbons have the potential to reduce the surface energy to the lowest values possible, where the long fluorinated chains of the chemical attach normal to the surface of the substrate. The repellency of the resultant finish depends on several factors such as the fluorinated and nonfluorinated segments, the orientation, the distribution of the fluorocarbon groups on the fibres and the composition and geometry of the fabric.

7.3.4 Testing water and oil repellency

Not surprisingly, there are numerous ways of measuring liquid repellency. Many of these have been developed by companies in order to deliver the specific product requirements their customers demand. Depending on the product and application, several testing methodologies may need to be applied to demonstrate that the right performance characteristics are delivered.

Table 7.2 lists some of the more popular water repellency tests that are available. These fall into three main categories: (i) spray tests, (ii) hydrostatic pressure tests and (iii) sorption of water tests.

Many requirements for fabric treatments state that air permeability properties need to be retained in addition to the 'hand' and 'drape' qualities. In these instances tests such as air permeability and water vapour permeability (ASTM D 737-96; DIN 53 887) are also required.

The main oil and water repellency tests for semi-quantitative measurements of surface energy involve placing three small droplets of graded test liquids onto the fabric surface, usually for 30 seconds for oil-based and 10 seconds for aqueous-based liquids. The droplets are removed using an absorptive tissue. If no wetting is observed on the fabric from two out of the three droplets, the next test liquid is used, and so on until wetting is observed. The highest value test liquid used where no wetting is observed

Table 7.2 Commonly-used water repellent tests for treated textiles

| Name | Test | Comments |
|--------------------|---------------|--|
| Spray test | AATCC 22-1996 | Developed by DuPont Co. Can be carried out without destroying the article. Difficult to differentiate fabrics with good water repellency |
| Sputter apparatus | AATCC 21-1998 | The lowest hydrostatic head needed to cause penetration is recorded. Normally used for fabrics coated with an impermeable film |
| Dynamic absorption | AATCC 70-1997 | Measures weight increase as a percent of water absorbed |

Table 7.3 Test liquids for oil repellency ratings

| Oil-repellency rating | Test liquid | Surface tension (mN/m)* |
|-----------------------|--------------------------|-------------------------|
| 1 | Nujol oil | 31.2 |
| 2 | 65/35 nujol/n-hexadecane | 28.7 |
| 3 | n-hexadecane | 27.1 |
| 4 | n-tetradecane | 26.1 |
| 5 | n-dodecane | 25.1 |
| 6 | n-decane | 23.5 |
| 7 | n-octane | 21.3 |
| 8 | n-heptane | 19.7 |

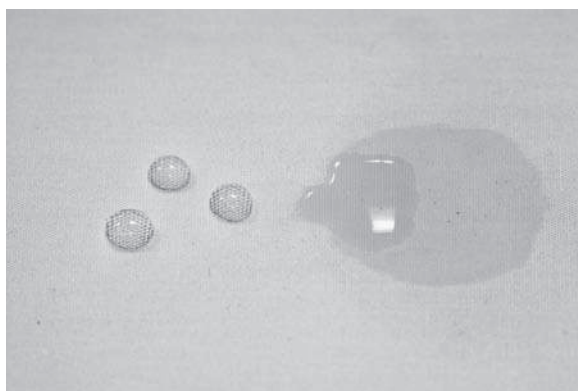
*Data by R. H. Dettre.

is the value given to the textile. The example shown opposite (Figure 7.3) is for the AATCC 118-1997 test method where the *oil* series of liquids ranges from Oil 1 (O1) – Oil 8 (O8), where O1 has the highest surface tension and O8 has the lowest, i.e. the easiest to repel and the hardest to repel, respectively (Table 7.3). As can be seen from the image, the value given to this material is O6. The range of *polar* test liquids are from W0 (100% water) to W10 (100% isopropyl alcohol), where W6 is composed of 60% isopropyl alcohol and 40% water. If the test sample fails the lowest water or oil repellency tests, a value of WF and OF can be recorded, respectively.

7.4 Current solutions for rendering textiles water and oil repellent

7.4.1 Introduction

Treatments for rendering textiles water repellent have been around for many years and the earliest involved using hydrophobic substances such as



Decane

Octane

7.3 Droplets of decane and octane on a fluorocarbon-treated fabric.

paraffin. Mixtures of wax or paraffin emulsions containing aluminium acetate have also been used. However, as explained earlier, in order to achieve both water and oil repellency, it is necessary to use fluorocarbon moieties.

The terms encountered when describing liquid protection for textiles are ones such as 'waterproof', 'water resistant' and 'water repellent'. All mean subtly different things, which can confuse consumers, and so below is a review of the more popular descriptions and what they actually mean.

Firstly, it should be noted that water, in one form or another, can penetrate most things; it is even used to cut blocks of steel. The determining factor is the pressure applied. To cut a block of steel using water jets requires a pressure of around 60 000 pounds per square inch (psi). Water in this form will rarely be encountered but it serves to show that, providing the force is high enough, water will break through virtually anything. Despite this, the term waterproof is often used where quite simply this refers to liquid protection that is fit-for-purpose. This means that a garment worn containing waterproof technology would expect to stay dry if subjected to the harshest driving rain or if the wearer sat down or knelt in water. The technology will protect you from the force of water likely to be encountered in that situation. Therefore, it can be agreed that different products would require different levels of waterproof-ness depending on the market demands. Water repellent refers to surfaces where water will not wet; however, providing the forces are great enough, they could drive the droplet through the material and the waterproof-ness is therefore a function of the porosity of the underlying material. Water resistant is another confused term and will be used by some industries to describe a surface that is not fully waterproof.

There are many potential situations where people expect to stay dry when the force of water is not very high; however, the product used will still be perceived to be waterproof. For example, running shoes take the majority of the force impact from water with the sole, which is impermeable. So, if running through a shallow stream or puddle, the fall-back of water onto the permeable upper material will have much less force and may not penetrate the shoe, which will therefore be perceived by the wearer as being waterproof.

The main issues of providing fit-for-purpose liquid protection comes down to a compromise between the level of protection provided and the physiological burden imposed. This means it is very easy to provide complete liquid protection to a person. However, the solution would involve completely dressing the wearer head-to-toe in a rubber suit; totally impractical as the wearer will soon tire and become unable to carry on due to the heat stress imposed. By providing just enough protection, greater wear comfort can be achieved, due to the greater breathability of the material. This leads to the necessity to fully segment a particular market to deliver what is required. For example, clothing suitable for harsh weather conditions will be more than likely inappropriate for brief periods of shower resistance, where a more suitable lower physiological burden garment can be provided.

Generally, waterproof fabrics are created by laminating a microporous, or hydrophilic polymer at the backside of the fabric. The reason being, the majority of fabrics are air permeable due to the nature of the weave which allows the desirable drape qualities as well as breathability. A consequence of this is that water can be forced through and so extra protection is required. For many applications where high performance is not required, i.e. no need to protect against a high *force* of water, more open weave structures can be used which are generally more desirable anyway, due to greater breathability which allows any heat and water vapour created by the body to readily pass out of the garment and cool the person wearing it.

There are numerous methods on the market for rendering textiles water and oil repellent, the majority coming under the general description of dip coating and spray coating. They are often referred to as DWRs (durable water repellents). The general consensus seems to be that there is no PWR (permanent water repellent) treatment that can be applied to products, as properties drop off over time, with laundry washing and/or dry cleaning.

7.4.2 Dip processing

The vast majority of processes fall under dip/solution-based coatings and have several factors in common:

- Process is applied to the textile in roll format before construction of the garment or end product
- Vats of complex chemical formulations are used, which not only contain the chemicals required on the textile to give the repellent effects, but many others required to allow the chemical to film-form and attach to the surface
- The vats used are of a particular formulation to attach specific chemical groups onto the textile, so other formulations are required to attach to different types of materials
- High temperatures are required to effect fixation, secure the groups on the surface and drive off the water/solvent required to apply the technical effect.

There are many different companies that provide their own trademarked formulations to achieve this effect and there are specific advantages and disadvantages of these forms of processing:

Advantages

- High through-puts available
- Cost-effective when processing in large quantities
- High levels of liquid repellency possible.

Disadvantages

- Not applied to the end product, therefore complete protection of the constructed product is not possible
- Expensive/unfeasible for small batches
- Cannot be applied to 3D forms and limited to textiles of specific chemical make-up
- Cannot be used as a re-coating process for the end product due to unfavourable solution energetics and incompatibility of product form.

7.4.3 Spray coatings

Again, a wide variety of products are available in the market place providing a range of both water and or oil repellency treatments. The general form of application is through an aerosol-can and, while good levels of protection can be provided, the main issues surround the durability of the treatment along with how much coverage has occurred and the amount of chemical that is lost into the environment.

There are many applications where solution-based dip or spray application is the most economical and present the best method of providing both water and oil repellency. However, like any technique there are inherent drawbacks, and it is because of these that people have looked to alternative technologies that overcome these drawbacks and indeed become benefits of the new process.

7.5 Use of plasmas for imparting liquid repellency

7.5.1 Introduction

As discussed earlier, there are some good advantages to using solution-based applications to render items liquid repellent, but due to inherent drawbacks, alternative technologies are being looked at and indeed have proven cost-effective in many industries where products processed via these new methods are being sold today.

One common problem of solution-based applications is the cost implications of heating vats of aqueous liquids to high temperatures, carrying out the fabric treatment and then using further energy to dry out the fabrics. Due to the general reluctance of using solvents for applying the technical effect and the cost implications of using aqueous based systems, a move away from solution-based processing is very attractive. However, the applicability of new technologies and the cost/performance relationship should be fully understood before embarking on large scale production. One such alternative would be the use of gas phase processing, which eliminates the requirement of having to remove a liquid post-treatment, in addition to numerous other benefits.

The first major challenge, which defines the type of gas phase process, is deciding how to activate the gas phase in order to create a reactive medium that can be used to treat the material of interest. One of the more common methods of activating a gas is through ionisation which produces what is more commonly known as the fourth state of matter and was referred to as a plasma back in 1929 by Langmuir.

7.5.2 Types of plasma

The most common methods of creating a plasma are corona discharge or dielectric barrier discharge, flame treatment and low pressure glow discharge; this is by no means an exhaustive list and the terminology is often confused. The techniques can be broadly broken down into two categories, atmospheric-pressure plasmas and low-pressure plasmas, and these will be addressed separately.

7.5.3 Atmospheric-pressure plasmas

One of the main attractions is undoubtedly the fast line speeds that are potentially possible. Providing the same technical effects can be achieved, in comparison to solution based processing, several advantages of plasma processing exist:

- High line speeds possible, leading to reduced unit cost
- Reduced equipment foot print, as vertical processing is possible
- Minimal environmental impact due to no large chemical vats required
- Can functionalise a wide variety of materials.

However, due to the nature of these processes, items are limited to flat sheets, webs and films that can be processed roll-to-roll and, in general, the final product will not be treated. While this is not always a drawback, it makes atmospheric-pressure plasma processes direct competitors to the solution based application methods. Because of this, the performance/cost relationships can be directly compared to address the feasibility of atmospheric-pressure treatment of textiles for water and oil repellency.

One of the main problems arising through atmospheric-pressure based processing used to obtain water and oil repellency, and indeed other functional effects, is the ability to retain the long chemical chains necessary to give the technical effect. Plasmas are inherently a destructive process and sophisticated processing is required to retain complex chemical groups. In addition, obtaining the required technical effect whilst achieving high line speeds is also a critical calculation in assessing the feasibility. Within the textile industry, fabric functionalisation is low down the value chain so costs need to be at a minimum and equipment sited with the relevant textile manufacturer or distribution warehouse. Another consideration is the management of waste materials that could contain toxic components. Atmospheric plasma processing is covered in Chapters 4 and 5 and these should be consulted for more in-depth information.

7.5.4 Low-pressure plasmas

Introduction

The information contained within this section outlines the benefits of low-pressure plasma processing, specifically addressing the experience encountered with the development of a process and the scale-up of a technology for making textiles water and oil repellent. It does not give an account of low-pressure plasma processing itself as this is covered in detail in Chapter 3. It will address the main challenges faced by scaling-up and providing a cost-effective, value-adding industrial process.

Background

The majority of low-pressure plasma processing systems are batch processes. There are a number of examples where continuous roll-to-roll processing is carried out within a batch process, i.e. there is down-time when changing between rolls as the whole roll is pumped down to low pressure,

and a few examples where fully continuous processing is possible through 'whistling leaks' where differentially pumped systems allow the constant transport of material. Batch processing is also possible on a continuous basis or on an in-line system, where samples can be loaded whilst pump down and processing occurs in other sections. Nevertheless, compared with continuous treatment with atmospheric-pressure plasma processing, the line speeds and initial capital costs initially appear unattractive. However, experience has shown that there are numerous technical benefits of operating at low-pressure, where even relatively modest through-puts can provide a cost-effective solution – provided that the technical effect adds sufficient value. The main features of processing at low-pressure are:

- Ability to treat complex 3D items including finished products and off-the-shelf items
- Items can be re-treated if necessary
- Process can be sited anywhere, can easily be integrated into a production line and can be applied anywhere along the value chain
- Process can treat a wide range of different materials at once
- Process gives greater control of the degree of ionisation and hence fragmentation of the starting material. This way raw chemical functional groups can be preserved and attached to the product
- Low amounts of starting raw chemicals are required. Not only does this lead to cheaper processing costs but negligible waste costs and environmental impact
- Depending on the items to be treated, fast through-puts can be possible by simply optimising the system for a particular product.

Nobody expects one process to be best for every application and volume demand; however, it is because of these features that it is believed low-pressure plasma processing can deliver considerable value to a wide number of products in numerous market areas.

Process development

Conventionally, low-pressure plasmas have been used as a means of fragmenting the process gases in order to achieve novel surface functionalisation and display a new range of features. Later, people started to look at using vapours from liquids and tried to maximise the retention of functional groups which could be used to subsequently react with other chemicals to obtain a specific chemistry. In order to achieve attachment of long fluorinated chains to the surface, critical for the levels of liquid repellency required, it was necessary to both select a chemical that displayed the necessary functional group, and to apply the right amount of energy; too much

would fragment the monomer and too little would not allow polymerisation to occur.

It was discovered that the best way to achieve the power required to initiate the plasma and create reactive intermediates, to allow conventional polymerisation to occur in order to retain the structure as much as possible, is to modulate the power through a pulse cycle. Through careful choice of starting chemical and optimisation of the plasma parameters to maximise the $\text{CF}_2:\text{CF}_3$ ratio, a pulsed plasma polymerisation process has been developed to provide high levels of both water and oil repellency, achieving repellency to both isopropyl alcohol and heptane on cotton samples. In fact, if very rough materials are used, repellency to hexane can also be achieved. The key is to generate the active species whilst allowing conventional free radical polymerisation to occur.

Results

Synthetic and natural fibres do not show any inherent repellency to oils. Some, particularly the natural fibres, may show a residual degree of hydrophobicity due to the natural oils within the product. However, as the surface tension of the test liquids begins to decrease within the polar series, wetting will soon occur and will usually happen at around 10–20% isopropyl alcohol content (W1–W2).

Several companies report that they can apply oleophobic properties to textiles through post-treatment, either through the use of plasma processing or by a solution-based approach: however, the level of oleophobicity obtained is harder to find. Table 7.4 lists the levels of both water and oil

Table 7.4 List of water and oil repellency values obtained on a variety of textiles. WF and OF represent failure at lowest level

| Textile | Untreated | | Plasma processed | |
|------------------------------------|-----------|-----|------------------|-----|
| | Water | Oil | Water | Oil |
| 100% cotton interlock | W1 | OF | W10 | O8 |
| 65% polyester 35% cotton | WF | OF | W10 | O8 |
| 65% polyester 35% cotton interlock | W1 | OF | W10 | O8 |
| Spun viscose woven | WF | OF | W10 | O8 |
| 50% cotton 50% polyester | WF | OF | W10 | O8 |
| Cotton sheeting | WF | OF | W10 | O8 |
| 100% cotton poplin | WF | OF | W10 | O8 |
| Polyester cross tuck | W0 | OF | W10 | O8 |
| 100% Nylon 66 cross-tuck | WF | OF | W10 | O8 |
| Wool | W1 | OF | W10 | O8 |

repellency obtained using the P2i process on textiles and this can be used as a comparison when other results using different techniques are known. The results illustrate the universal attachment of the chemical groups to a variety of different materials, displaying the highest levels of repellency, all of which were processed in the same chamber run.

Another value that is also reported is the surface energy where two factors are particularly important: (i) the sample should be flat because surface roughness plays a major role in enhancing contact angles and (ii) the test liquids selected need to assess the functionality desired. This latter point means that if one seeks to determine the level of oil repellency, it is necessary that oils are used to test the surface. Methylene iodide has been widely used to calculate the surface energy and determine the degree of oleophobicity; however, it does not resemble oil. Methylene iodide should therefore only be used to benchmark different surfaces reported in the literature and a homologous series of hydrocarbons to probe the level of oleophobicity should be used.

Scale-up challenges

The author's original work in obtaining a high level of both water and oil repellency was carried out in a 470 cm³ (~0.5 litre) quartz reactor. The next steps were to scale-up the process to provide a cost-effective, value-adding industrial process. The chamber volume was therefore subsequently increased to 3 litres and then 40 litres, both using the same set-up as the original system, with the biggest challenge being how to reduce the pump-down time to an acceptable level. As the amount of textile increases, the amount of water that needs to be removed to reach an adequate base pressure increases and the pumping conductance needs to be taken into consideration.

The first major scale-up step was to a plasma chamber with an internal processing volume of around 300 litres. The major technical differentiators were:

- Stainless steel chamber with internal capacitively coupled electrodes
- Large vacuum pump capacity for evacuating the chamber as quickly as possible
- Alternative monomer inlet system to ensure required processing pressure.

By increasing the conductance of the pipe work between the pump stack and the chamber, shorter pump down times could be ensured. However, with a full loading of textiles, pump-down times could still be lengthy due to removal of water absorbed by hydroscopic materials. What needs to be determined is the base pressure – processing vapour pressure – product

out-gassing relationship to ensure that the polymer deposits effectively onto the product without being 'poisoned'.

Although the increase to 300 litres represents just over a seven-fold scale-up on the previous chamber, using the process to treat textile products is only cost-effective for very high added value items, where performance reigns over cost. A further scale-up was required in order to cope with the demands of the garment and accessories industries, where numerous items could be processed at once. The next processing volume chosen was 2000 litres, to prove that the process could be applied to fully constructed items and treat a wide range of items in sufficient quantities to be able to carry out market trials to benchmark the technology (Figure 7.4).

The chamber has shown many similarities to the 300 litres system and has demonstrated a high degree of homogeneity with regards to the levels of liquid repellency on cellulose substrates and textiles such as polyester.



7.4 P2i's 2000 litre plasma chamber.

Commercialisation

Processing costs can be competitive, despite the equipment costs. To maximise return on the investment, systems need to operate throughout the day.

When analysing the through-put, there are seven main time-related tasks which cumulatively give the total processing time:

- (i) loading of samples
- (ii) pumping down to base pressure
- (iii) introduction of gases and vapours
- (iv) ignition of plasma and processing
- (v) turning off plasma power and gases
- (vi) evacuating chamber back to base pressure
- (vii) venting up to atmosphere and unload.

Tasks (ii) and (iv) are the most time-consuming and need to be reduced as much as possible whilst still achieving the technical requirements. It is quite possible to achieve a total turn-around time of one hour or less.

Durability

Durability often provides an interesting discussion, since all products have different durability requirements. When durability is mentioned, people are often referring to laundry wash durability, dry cleaning or abrasion resistance. However, the number of cycles required varies vastly across the industry. Laundry wash durability is more challenging than durability to dry cleaning cycles, where independent tests on the latter have shown that the pulsed plasma process developed by the author's company could achieve, at its first attempt, the same level of repellency as a leading benchmark for solution-based applications. Further improvements are believed possible once optimised. Mechanical durability has also shown very good comparisons with industry standards where, although some drop off is noticed, very good oil and water repellency is still provided.

7.6 What the future holds

Plasma treatment of textiles for water and oil repellency is both feasible and is currently being used to process a number of products that are either in the later stages of development or already in the market place, proving this is a cost-effective industrial process.

Further optimisation is required to make ever cheaper, automated equipment that will greatly increase the appeal of this technique. In addition, to expand the number of commercial applications, the processing volume of equipment will need to be scaled-up further.

The low-pressure plasma technique for imparting high levels of liquid repellency to textile products has already entered the commercial age due to its added-value performance and its processing and environmental advantages. The next few years will see this become a widely established, cost-effective industrial solution.

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Interfacial engineering of functional textiles for biomedical applications

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8.1 Introduction

Textiles for clothing increasingly offer special functionalities, such as hydrophobicity, soil release, breathability, UV-stability, flame-protection, antibacterial and antistatic properties. These technical textiles are used, in particular, for outdoor sports, and protective and safety clothing. Other technical textiles include geotextiles, and textiles for architecture, vehicles, transport and packaging. Textiles for medical and healthcare are another well-known industrial sector, with increasing market potential (Rajendran, 2002).

Biomedical textiles must be designed to meet a range of requirements, including minimising non-specific protein adsorption, biocompatibility (blood-, cyto- or tissue-compatibility), and the presence of active functional coatings, such as antibacterial finishes, bioactive layers or drug delivery systems. To achieve these properties, tailor-made surfaces are needed that do not alter the bulk properties of the polymer material used. Sometimes only one type of chemical functionality is required, e.g. carboxyl- or amino-groups homogeneously distributed at a defined density over the total surface area. For some products or production lines, the use of toxic or hazardous chemicals must be avoided. To achieve these requirements, low-pressure plasma functionalisation may be the method of choice.

In this chapter, Section 8.2 gives a brief introduction to technical textiles for biomedical applications and Section 8.3 introduces plasma-based techniques. Different methods for activation, functionalisation, grafting and polymerisation are explained, together with the interaction between plasma and textiles. Specific functionalisation retaining the monomer structure will be examined in detail. In Section 8.4, some technical aspects of experimental set-ups and industrial plants are given, and Section 8.5 deals with assessing the treated samples. Examples of plasma-finished biomedical textiles are given in Section 8.6, and the final section looks at applications and

products under investigation or currently on the market, together with an overview of future trends.

8.2 Technical textiles for biomedical applications

Technical textiles are one of the faster-growing sectors of the global textile industry, with the industry moving rapidly toward the manufacture of high added-value textile structures and products, including medical textiles, protective textiles and smart textiles. Textiles used in the medical and applied healthcare and hygiene sectors are an important and expanding part of the industry, and are often referred as to biomedical textiles.

According to Rajendran (2002), four categories of medical textiles can be distinguished:

- non-implantable materials
- implantable materials
- extracorporeal devices and
- healthcare and hygiene products.

Medical and healthcare products demonstrate a remarkable range of applications, from simple bandages to biocompatible implants and tissues, antibacterial wound treatment material, prosthetics and intelligent textiles. The different fibres, mono- and multi-filament yarns, woven, knitted, non-woven, and composite fabrics for manufacturing various medical products, are summarised within these four categories in Rajendran (2002).

A biomedical textile is designed according to its final function. The main factors to consider include:

- *Function*: The textile must fulfil the purpose for which it was designed, for example, swabs must be absorbent, sutures may need to be biodegradable, hospital bedding should be comfortable and durable.
- *Cost*: This will depend on the raw materials, manufacturing process and product end-use. Surgeons' gowns and swabs should have a low production cost, while vascular grafts and artificial skin can have a relatively high production cost.
- *Product approval*: Each country has its own regulations and standards for medical textiles. The European Union has introduced Community Legislation to govern medical devices. The three Directives are: Active Implantable Medical Devices, Medical Devices and *In-Vitro* Diagnostic Medical Devices.
- *Biocompatibility*: This refers to possible reactions of the textile with blood and tissue in the body. An implantable device has greater potential for reaction than an external device and is, therefore, subject to tighter regulations. For example, an artificial ligament is permanent and

internal, so will come into contact with blood cells and the surrounding tissue, whereas an external bandage is temporary and only comes into contact with the outer skin.

The definition of biocompatibility according to the European Society for Biomaterials, is: 'the ability of a material to perform with an appropriate host response in a specific application' (Williams, 1987). It is important to recognise that this definition focuses on a 'specific application'. A specific application imposes requirements on particular properties of the material. This could be bulk properties, such as mechanical strength, or surface properties, such as the surface energy (wettability) or the presence of special functional groups. The second major point in the definition, 'host response', is more complex and embraces the interaction at the interface between biomaterials and tissues, cells (cyto-compatibility), blood (haemo-compatibility) and biological responses such as inflammation, thrombosis and healing (Ratner, 1990). Undesired host reactions are mostly driven by surface/protein interactions. Such protein adsorption occurs on first contact with biological fluids and tissues (Hubbell, 1995a). The nature and amount of the protein adsorption layer depends on the material surface properties, including wettability, polar or ionic interaction, chemical structures and topography of the surface. A good review dealing with the topographical control of cells is given by Curtis (1997). The influence of wettability, hydrophilic or hydrophobic interaction of biomaterials (proteins, cells, etc.) with material surfaces is discussed in detail in an outstanding review by Vogler (1998). Protein adsorption can also be desirable and indeed a prerequisite, for instance for improved cell adhesion and subsequent cell growth as needed, for example, in tissue engineering (Keselowsky, 2005). It is therefore imperative to design and tailor the surface properties of medical textiles according to the intended application.

Tailoring the surface properties of polymer materials such as foils, films, fibres, fabrics, non-wovens, etc. can be achieved by wet chemical treatments or physical techniques such as glow discharge plasma treatment. Systematic investigation of plasma polymerisation started in the 1960s (Goodman, 1960). Plasma-based surface functionalisation is today accepted as an important process for the formation of entirely new materials, and as a valuable technique to functionalise the surfaces of polymers or other materials. Within the last two decades, large improvements have been made in reactor design, the understanding of energy input (continuous wave or pulse techniques), and the polymerisation of monomers while retaining their monomer structure (chemical functionality), making this technique applicable to the development of medical textiles.

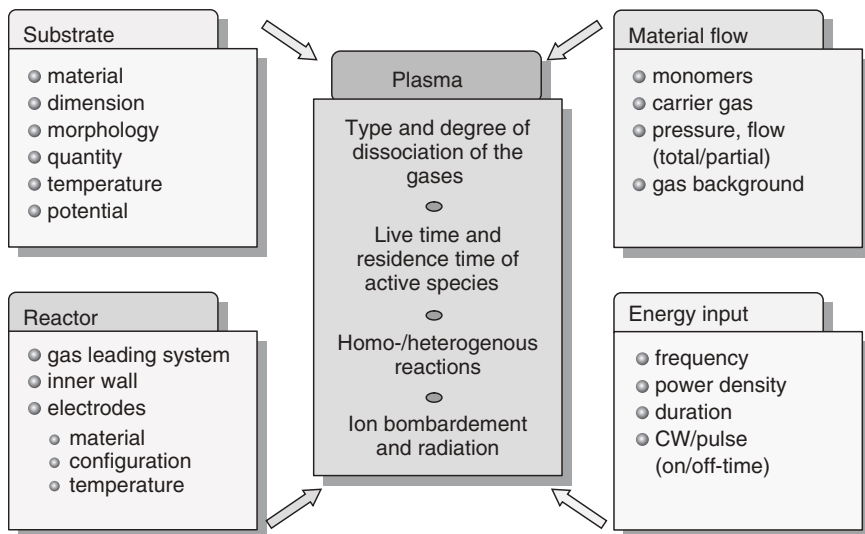
8.3 Plasma treatment for interfacial engineering of technical textiles

The main advantages of plasma treatments are:

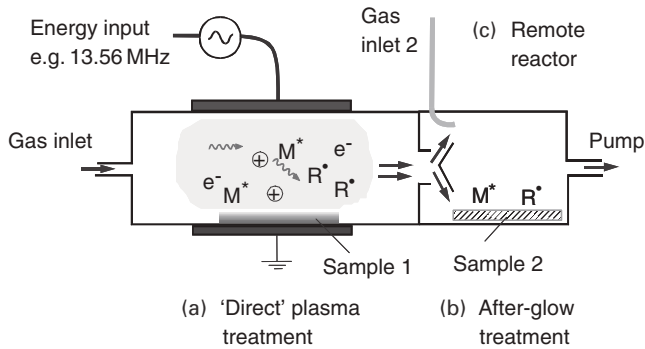
- Modification is limited to the top surface layer and does not affect the bulk properties of the polymer
- Modification by plasma processes is largely independent of the structure or chemical reactivity of the substrate
- A broad range of functional groups can be introduced at the surface, by varying the monomer gas used
- The modification is generally fairly uniform over the whole substrate and
- Plasma treatment is an all-dry process.

The principles of low-pressure cold plasma and atmospheric-pressure cold plasma processes have been described in detail in Chapters 3 and 4, respectively. This chapter provides a brief introduction to low-pressure glow discharge treatment using radio frequency (RF) excited discharges.

The major parameters for this process are shown in Figure 8.1. By varying these parameters, three completely different types of surface modification are possible, etching, functionalisation and coating. Further variations are made possible by altering the treatment conditions of the material itself, such as treating the material directly in the plasma zone, in after-glow or



8.1 Plasma parameters influencing the plasma conditions.



8.2 Schematic view of three different plasma techniques. (a) direct plasma treatment (b) remote technique; the treated samples is positioned outside the direct plasma zone in a second chamber (c) after-glow technique; the polymerisable monomer gas is introduced in the remote zone.

remote plasma, and by using plasma grafting processes (see below). Figure 8.2 gives a schematic view of these process types.

With RF excited discharges, different implementations are possible, such as inductively (ICP) or capacitively coupled plasmas. With ICP, internal or external electrodes can be applied (Hegemann 2005a). Textiles can be treated with or without plasma gas flux through the porous structure of the fabric (Oehr, 1995). To summarise, plasma-based techniques are marked by a great variety of process possibilities, so that processes can be optimised for the desired application of the product. Plasma processes can be developed for almost any surface functionalisation in research laboratories. The challenge is to scale-up laboratory parameters to cope with the typical sizes and speeds needed for industrial operations.

8.3.1 Plasma cleaning/plasma etching/sterilisation

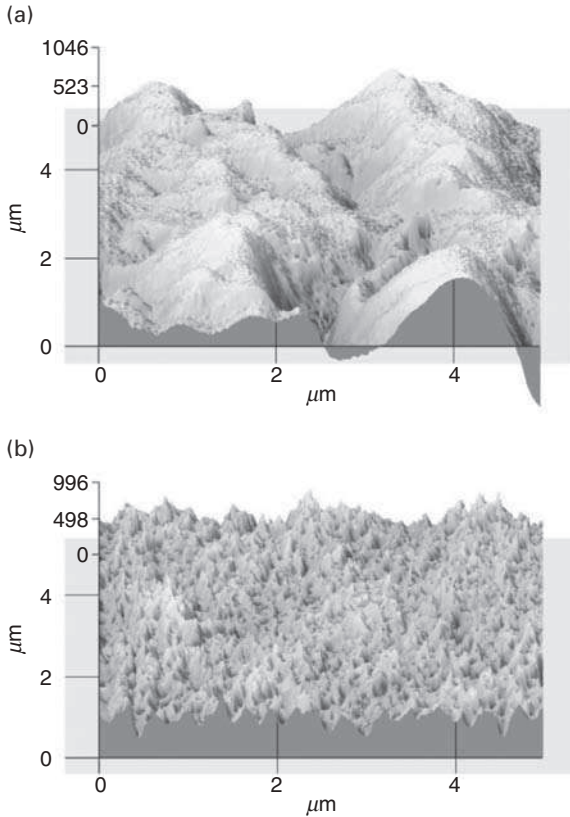
Polymer surfaces can be cleaned or etched, mostly using non-polymerisable gases such as O₂, N₂, H₂, the noble gases or gas mixtures. In the past, plasma etching was mainly used to etch textile fibres to increase tensile strength or resistance to felting shrinkage (Thorsen, 1974; Rakowski, 1989). Etching conditions for plasmas have been used to remove contaminations (lubricants, oils, surfactants, etc.) for decades (Vohrer, 1997). This technique is also important for biomedical applications to some extent, because it can be used to remove thin surface coatings that might otherwise be responsible for inflammatory reactions on contact with cells (Chinn, 1998). Etching has also been shown to promote improved cell attachment in tissue culture studies (Amstein, 1975). Etching is also associated with an increase in wettability (Oehr, 2000).

Sterilisation is a specific method of cleaning. Sterilisation refers to the complete inactivation of all infectious agents. Plasmas have been implicitly assumed to possess sterilisation properties (Boucher, 1985). The mechanisms of plasma sterilisation were analysed in terms of the action of UV emission and interaction with radicals produced in the plasma. A review of the mechanisms of plasma sterilisation can be found in Lerouge (2000). The resulting sterility must be assessed because different micro-organisms and their spores show different mortality rates. *Bacillus subtilis*, *Bacillus pumilus* or *Bacillus stearothermophilus* spores are commonly used (Vohrer, 1999; Lassen, 2005). Plasma sterilisation is often referred as a low temperature technique, compared to water vapour sterilisation, the former therefore having advantages for the sterilisation of thermo-labile polymers. However, low temperature is not necessarily an accurate description. The sterilisation of, for instance, radiation-stable micro-organisms such as *micrococcus radiodurans*, or high concentrations of spores, can require high energy inputs and long treatment times, which can cause a temperature increase in the substrate up to the melting point of the polymer. This problem was overcome for removing mildew contamination on cellulose fibres (ancient documents) by optimising the process, with an additional increase in paper strength. After-glow hydrogen plasmas are the method of choice (Vohrer, 2001).

Plasma-based etching can change the surface roughness of polymers, and this should be taken into consideration. Figure 8.3 shows AFM pictures of polyethylene before and after oxygen plasma treatment. A dramatic change in the micro-roughness can be seen. Depending on the plasma conditions, similar results can be found on other polymers (see e.g. Wong, 2000). For the textile industry, this effect could be used to generate an anti-pilling finishing, for instance in wool (see Chapter 9). The alteration in surface morphology can also influence blood or cell interaction (see below). The use of non-polymerisable monomer gases not only removes material from the surface and alters its topography, but also leads to a change in chemical composition. For instance, if oxygen is used as the process gas, a great variety of different oxygen-containing functional groups, such as $-\text{OH}$, $-\text{C}=\text{O}$, $-\text{COOH}$, will be introduced onto the surface of the material. This is generally referred to as 'unspecific' functionalisation. Nevertheless, this is an important industrial process, used mostly to increase the adhesion properties of materials (Strobel, 1994; Erli, 2003) or the dye-uptake and printability of textiles (Wakida, 1993).

8.3.2 Plasma functionalisation/plasma grafting

The main goal of plasma functionalisation is to create a tailor-made surface with a specific function. Several applications require only one type of



8.3 AFM-picture of polyethylene before (a) and after (b) an oxygen plasma treatment. After the treatment, the micro-roughness of the sample is dramatically changed.

functional group ($-\text{COOH}$, $-\text{NH}_2$, $-\text{OH}$, $-\text{CHO}$, epoxy, etc.) to be added to the material surface, and are typically needed for applications in the medical and pharmaceutical field (Oehr, 2003). The functional groups on the surface serve as anchoring sites for bioactive molecules such as growth factors, biolinkers, peptides and enzymes. Specific plasma functionalisation can be obtained by using monomer gases carrying the desired functional group, mostly combined with a double-bond ($-\text{CH}=\text{CH}-$) that easily generates radicals under plasma conditions, or a ring structure that opens during the plasma treatment. Monomers used include acrylic acid (AAc; carboxyl groups, Alexander (1998)), glycidylmethacrylate (GDMA; epoxy groups, Tarducci (2000)), 2-hydroxyethyl methacrylate (HEMA; hydroxy groups, Tarducci (2002)), and diaminocyclohexane (DACH; amino groups, Gölander (1993)).

The main problem when introducing monomers into the plasma zone of the reactor is the fragmentation of the monomer itself. This can be avoided

by using mild plasma conditions, such as low plasma power or pulse-plasma techniques. Since the 1990s, pulsed plasmas have been used to retain the chemical structure of the precursors in functionalisation and thin film deposition for medical engineering and for biological applications (Gombotz, 1987; Oehr, 1999). Another technique that retains the monomer structure is usually referred to as plasma grafting. In this method, free radicals are formed on the polymer surface as a result of inert gas plasma treatment. The radicals obtained then react with monomer gases that are introduced consecutively into the treatment chamber. This technique has been used for several decades, see, e.g. Simionescu (1984) and Kato (2003). Teichmann (1975) summarises different activation techniques for grafting onto textile fabrics. Plasma grafting leads to a thin-film coating of the substrates.

Plasma fixation is another method. Here, the textile is covered with a liquid monomer via dip- or spray-coating and the monomer is fixed to the surface by a consecutive plasma process, mostly using inert gas plasmas with argon or helium as the process gas.

8.3.3 Plasma polymerisation/plasma coating

Plasma polymerisation can be defined as ‘the formation of polymeric materials under the influence of plasma’. Solid deposits from organic compounds formed in a plasma, generated by some kind of electrical discharge, were described as early as 1874 (de Wilde, 1874). However, at that time very little was known about polymers, and these deposits were considered to be nothing more than undesirable by-products of the phenomena associated with electrical discharge.

The elemental reactions that occur during plasma polymerisation include fragmentation of monomer molecules, the formation of reactive sites (radicals), and recombination of the activated fragments. The mechanism follows similar steps to traditional radical polymerisation, with the possible inclusion of a re-initiation step. Plasma polymerisation to deposit a thin polymer film on the surface of a material can be done using nearly any organic, organosilicone or organometallic vapour. The substrate material, the application and hence the necessary properties, decide the choice of monomer gas. Treatment time influences the thickness of the applied coatings. There are a number of books dealing with plasma polymerisation; see, for instance, Yasuda (1985), Biederman (1992), and Inagaki (1996).

8.3.4 Plasma functionalisation retaining the monomer structure

Direct and indirect methods are used to introduce well-defined functionalities using monomers while retaining their structure. In direct methods, the

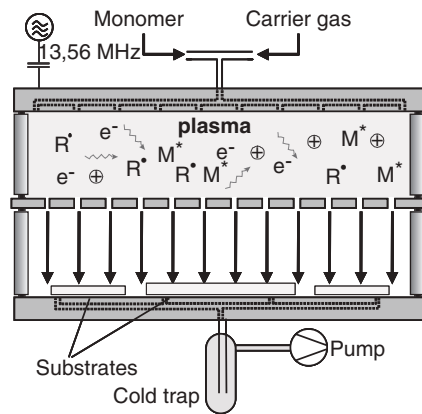
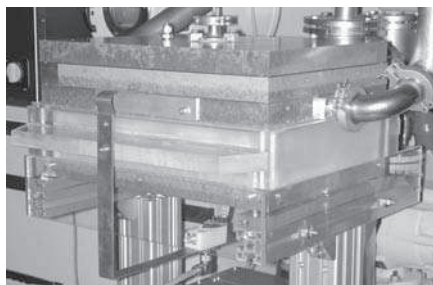
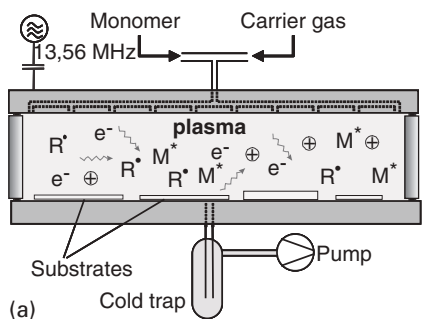
monomer is exposed to very mild plasma environments. For indirect methods, only the substrate is activated and exposed to the monomer after plasma treatment (grafting).

In 1971, Westwood found that plasma polymers possessed a chemically better-defined structure and composition if low power input was used during direct plasma treatment (Westwood, 1971). Pulsed low-power plasma helps avoid excessive monomer fragmentation in the plasma phase and reduces the amount of plasma-induced damage in the polymer. Pulsed plasma polymerisation was introduced first by Tiller (Meisel, 1972), continued by Yasuda (1977), and further developed by a variety of research groups (e.g. Panchalingam, 1993; Kühn, 1999; Oehr, 1999).

To retain the monomer structure during direct plasma processing, the main parameters are low power input (continuous wave or pulse), high working pressure (low mean free path), short treatment time for the molecules in the plasma, minimised ionic bombardment of the surface, and substrate cooling. An early attempt to describe the possibility of structure retention was given by Yasuda, who used an external parameter W/FM to express the plasma energy density, where W is the power input, F the flow rate and M the molecular weight of the monomer (Yasuda, 1978). Smaller so-called Yasuda factors correspond to less fragmentation, so monomers with higher molecular weights in a homologous series are less fragmented than those with lower molecular weights. Unfortunately, with increasing molecular weight, the vapour pressure decreases, and dosage of the monomer becomes much more difficult.

8.4 Plasma reactor techniques

Figure 8.4 gives a schematic view of the DIN-A3-reactor (size $30 \times 40 \text{ cm}^2$; DINA3), designed and developed at the Fraunhofer IGB for the optimisation and development of plasma processes. This laboratory-scale set-up represents a modular concept with symmetrical electrode arrangement and capacitively coupled RF-discharges. This apparatus enables the use of different gas flow regimes within the reactor and for the distance between the electrodes to be varied. The upper version in Figure 8.4 enables gas feeding and pumping on one side, whereas the lower version supports homogeneous 'flowing through'. A V/I-probe (ENI Model 1065) can be attached to the reactor to measure the applied voltages and current, which, among other things, aids in adjusting the energy input, especially at low power. In such laboratory-scale systems, the best parameter set for a particular process can be determined. For some biomedical applications, this reactor size is sufficient. For textile applications, larger treatment chambers that enable finishing from roll-to-roll are required. Figure 8.5 shows three different sized systems. At Fraunhofer IGB, a strip width of 18cm can be handled. At



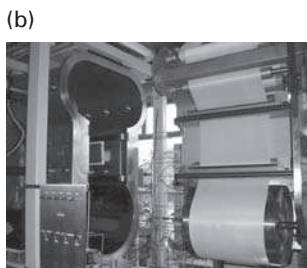
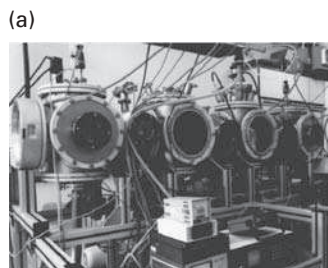
(a)

(b)

(c)

(d)

8.4 Schematic drawings and photographs of the modular, symmetrical reactors for plasma treatment, functionalisation and coating. The upper part represents a design with gas feeding and pumping at one side. The lower part represents a combined reactor with the possibility of direct plasma treatment in the upper chamber and after-glow treatment in the lower chamber.



(a)

(b)

(c)

8.5 Photos of three plasma roll-to-roll treatment systems. All systems enable a batch treatment. (a) Fraunhofer IGB strip width 18 cm (b) Empa strip width 120 cm (c) FZM Flöha (Niekmi, Russia) strip width 180 cm.

Empa in St Gallen (Hegemann, 2005c) and FZM in Flöha (Poll, 1998; Fuchs, 1999), larger systems are available.

To obtain good penetration of the gas flow into and through the textile structure, Oehr *et al.* (1995) described a system in which the gas flow was forced through the textile. Similar investigations are also found in recent publications (Verschuren, 2005).

8.5 Assessment of the functionalised textiles

The characterisation of plasma-treated textiles is described in detail in Chapter 12. This section is concerned with some general thoughts as well as some specific information regarding the assessment of biomedical textiles.

Polymer materials used in the biomedical sector must satisfy various requirements. To verify these properties, several analytical methods are used before and after chemical and mechanical stressing. Thin plasma polymer coatings have to be stable not only in typical solvents but also, if necessary, in biological liquids such as blood or cell culture medium. It is also extremely important to assess any possible immediate interactions with the respective biological system. The biological response is judged from tests, with cytotoxicity sensitisation, irritation, acute, chronic or subchronic toxicity, gene toxicity, haemocompatibility and carcinogenicity being among the most important. The tests applied depend on which type of contact is intended, and the duration of the contact and on the relevant national legislation. The US mandatory FDA norms are generally the determining model.

As mentioned in Section 9.3, plasma treatment can change the morphology (topography) of the polymer material, which may increase the specific surface area. Topography changes are normally investigated using the atomic force microscope (AFM). Any alteration in specific surface area can be analysed from adsorption/desorption isotherms (BET surface area). Changes in the wettability of textile fabrics can be measured via increases in hydrophilicity or hydrophobicity. Hydrophobicity is normally assessed by contact angle measurement, or using well-known textile tests such as the spray test (AATCC 22-1974), Bundesmanntest (DIN 53888) or even the oil repellency test (AATCC 118-1972). To assess hydrophilicity, the captive bubble method is mainly used. Suction tests and capillary rise tests are other methods for assessing the wettability of plasma hydrophilised textile samples (Hossain, 2006; Ferrero, 2003).

As mentioned above, it is important to assess the chemical functionality obtained after treatment. Depending on the film thickness, density and type of chemical functions, several sensitive analytical techniques can be used. Infrared spectroscopy (FTIR), X-ray photoemission spectroscopy (XPS;

ESCA), mass spectroscopy (TOF-SIMS), energy dispersive X-ray analysis (EDX; in combination with scanning electron microscopy, SEM) are some typical techniques.

The lateral distribution of functional groups in surface-treated or modified polymers may also play an important role in determining the interfacial properties of these materials. In biomedical applications, the functional groups must be distributed homogeneously to obtain biocompatible polymeric coatings. Determining spatial distribution and characterising the local environment on a sub-100 nm scale remains extremely difficult, if not impossible, even with the latest analytical techniques.

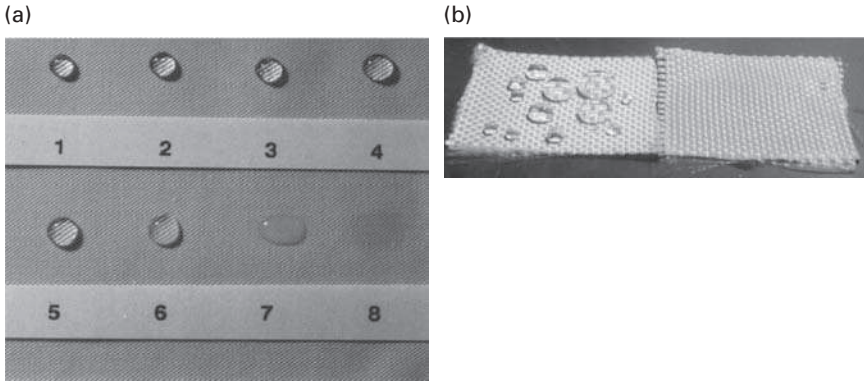
8.6 Surface engineering of biomedical textiles

As mentioned earlier, biomedical textiles are designed according to their function and need for biocompatibility, both of which are dominated by surface properties. Five examples of surface engineering in biomedical textiles are given below.

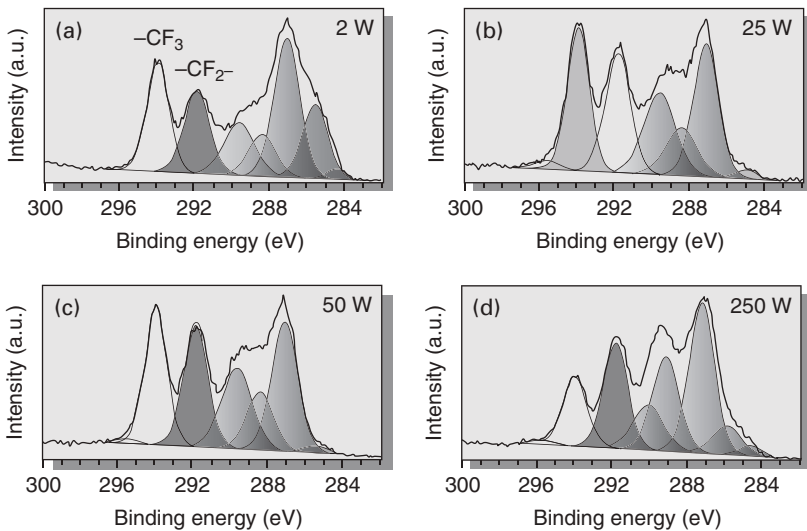
8.6.1 Example 1: Stain-repellent finishing

Hydrophobic and oleophobic stain-repellent textiles are used in leisure suits, safety clothes and surgical gowns, but there is also strong demand from the textile industry for other uses. Although wet chemical hydrophobic treatments such as Scotchguard® finishing are well established, plasma-based treatments are of interest because they use smaller amounts of chemicals and are therefore more environmentally friendly. Plasma grafting and plasma polymerisation have been investigated to assess their suitability for textiles finished with anti-soil, soil-release, and water or oil-repellent finishings. Byrne *et al.* (1972) used acrylic acid, allyl alcohol, vinyl fluoride, 1,1, difluoroethylene and tetrafluoroethylene in RF glow discharges. Millard *et al.* (1972) described a continuous low-temperature discharge treatment to give wool oil repellent properties. Lee *et al.* (1975) used perfluoroacrylates under discharge, after-glow and grafting (after oxygen or hydrogen plasma activation) for oil-repellent finishing in wool.

Fibres that contain water yield an outgassing during low-pressure treatments (Barni, 2003). This water participates in the plasma processes, resulting in the presence of hydrophilic functions on the treated surface. Good hydrophobic or even oleophobic properties can only be achieved by drying the textile prior to plasma finishing (Vohrer, 1998). Figure 8.6a shows an oleophobic finished cotton/polyester fabric with a 7C/8D evaluation, assessed by the 3M oil-repellency test (AATCC 118-1192). Figure 8.6b depicts an aramid fabric after plasma-based hydrophobisation, using



8.6 (a) Cotton/polyester fabric oleophobic finished via plasma-based treatment with perfluoroacrylates. Assessment of the oil repellency in accordance with AATCC 118-1992. (b) Hydrophobic finished aramid fabric. Left side treated, right side untreated.



8.7 C1s-ESCA-Spectras of hydrophobised cotton textiles using different plasma parameters. The increase in $-CF_2-$ groups can be triggered by the adjustment of the plasma conditions.

perfluoropropane as the process monomer. The left side is treated, the right side is untreated.

To optimise the process parameters, assessing the plasma conditions, e.g. via a V/I-probe, optical emission spectroscopy or laser-induced fluorescence, is as important as assessing the treated textile itself. In addition to the textile tests, surface analytical techniques are also needed. Figure 8.7

shows C1s-ESCA-spectras of plasma-hydrophobised textiles under varied plasma parameters. The spectra represents —CF_3 groups at a binding energy of 293.5 eV and $\text{—CF}_2\text{—}$ groups at a binding energy of 291.5 eV, respectively. Changes in the plasma condition alter the quantitative amount of —CF_3 and $\text{—CF}_2\text{—}$ groups, which are necessary for the hydrophobic property. Angle resolved ESCA-measurements demonstrate that, after process optimisation, the —CF_3 groups are terminal bonded and consequently located on the outermost surface (Barz, 2005). This is important for a good hydrophobic effect.

Although much research into the plasma-based hydrophobisation of textiles has been carried out (see also Chapter 7), improvements have generally been insufficiently economical to permit commercial adoption, with a few exceptions. This can be traced back to a lack of industrial-sized plants, but mostly to the need for oxygen and water-vapour free atmospheres during the fluorination of the plasma, and the need to clean the treatment chamber regularly. Recent developments emphasise a faster and more controllable hydrophilisation process prior to a common wet-chemical fluorocarbon impregnation. Plasma activation in a low-pressure RF discharge with Ar/O_2 was found to support subsequent wet-chemical impregnation due to enhanced capillary transport (Hegemann, 2005b).

8.6.2 Example 2: Biocompatibility/optimised cell growth

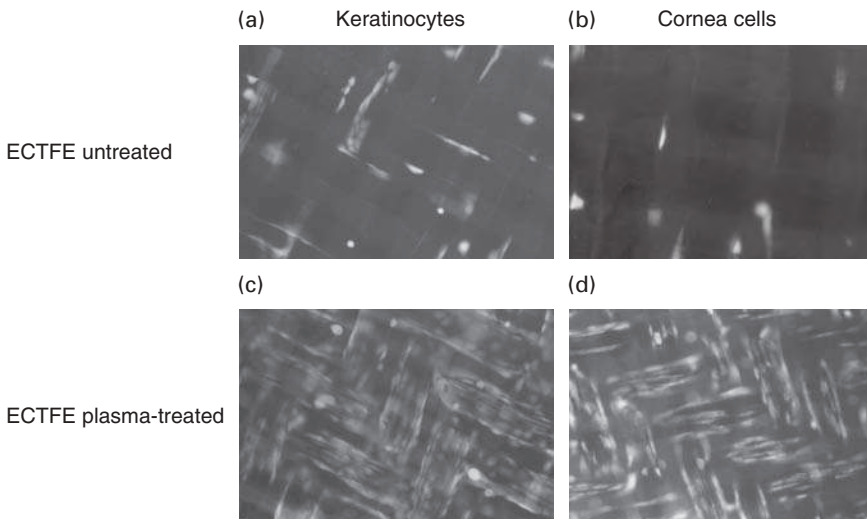
In the early stages of cell attachment, cell–substrate interactions are likely to be a function of the substrate surface chemistry (Wan, 1997), with optimum cell attachment to surfaces with low to moderate levels of hydrophilicity (Lydon, 1985). Cells normally attach to substrates via surface receptors on the cells, which interact with proteins adsorbed onto the surface of the substrate (Hubbell, 1995b). These proteins are adsorbed from either the surrounding serum (culture medium or biological fluid), or secreted by the cells themselves (Saltzman, 1997). Adhesive proteins are said to act as bridging molecules between the cells and the substrate (Lamba, 1998). Due to the hydrophilic and hydrophobic nature of proteins, substrates with an intermediate wettability at the surface usually show maximum cell attachment. Hydrophobic surfaces strongly denature adsorbed proteins (Sigal, 1998).

Cells interact with extra-cellular matrix (ECM) proteins. The biological activity of proteins on the surface will depend upon whether specific active peptide sequences in particular proteins are accessible to the arriving cells (Yamada, 1999). Many of the ECM proteins, such as fibronectin, carry a sequence of amino acids to which cells can bind using specific surface receptors called integrins. Integrin-mediated binding of cells is the foundation for cell growth and differentiation, and the dominant mechanism by which

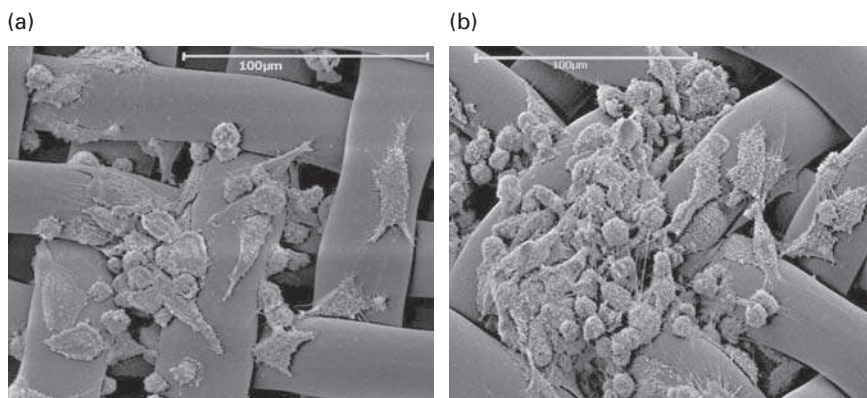
cells communicate with non-cellular surroundings (Ruoslahti, 1991). Different functional groups at the substrate surface alter the integrin binding and cell adhesion capability (Keselowsky, 2005), with COOH and OH groups showing greater cell adhesion than CH₃ (Tidwell, 1997). Other substrate properties thought to enhance cell adhesion are positively charged surfaces (Saltzmann, 1997) and grooved surface topographies, which may be due to an increase in surface area (Walboomers, 1999). Polymeric surfaces can undergo conformational rearrangements in response to environmental conditions, and can also exhibit differences in surface roughness and topology depending on process or surface modification (Tyler, 1992). Liu (2005) highlights some of the recent advances in understanding how environmental cues, presented through cellular adhesion, regulate cellular processes such as proliferation and differentiation.

By using glow discharge plasma techniques, the surfaces of different materials can be finished with specific functional groups. The combination of plasma techniques with wet chemistry treatment leads to biomaterials that optimise cell growth. For instance, to enhance corneal epithelial cell attachment and growth, an ammonia plasma treatment has been applied to artificial corneas fabricated from poly (hydroxyethyl methacrylate) (Sipehia, 1993).

Figure 8.8 shows the growth of ceratinocytes and cornea cells on a technical textile (ECTFE) before and after oxygen plasma treatment. Before the plasma treatment, only a few cells attach and are cultured on the textile. The increase in cell growth can be linked to an increase in wettability and



8.8 Growth of ceratinocytes and cornea cells on a technical textile before and after a plasma treatment.



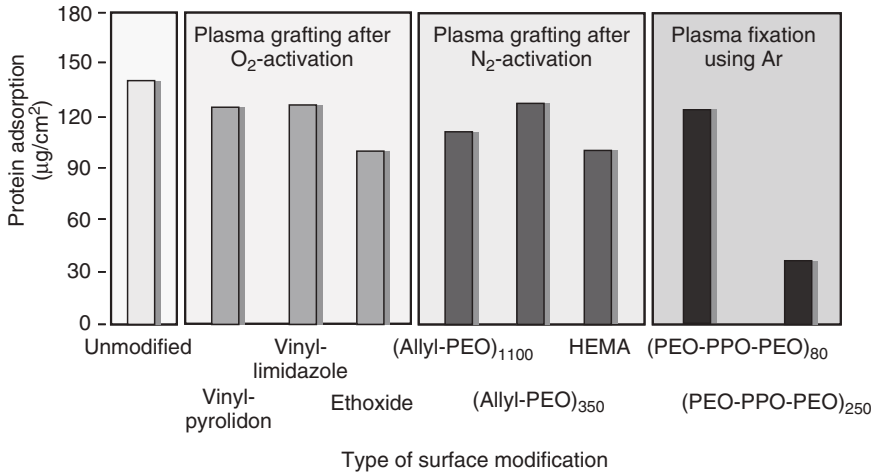
8.9 SEM pictures of stem cells attached onto a polyester fabric after plasma.

the introduction of oxygen-containing functional groups. The attachment of cells is the first step for cell culturing on substrates. Figure 8.9 shows scanning electron microscopy images of stem cells attached onto a plasma-modified polyester fabric.

8.6.3 Example 3: Biocompatibility/unspecific protein adsorption/biofouling

As mentioned in Example 2, contact of synthetic materials with biological fluids leads instantly to an unspecific adsorption of proteins onto the material surface. In most applications, this is undesirable because bacteria cells will also adhere to the material surface due to proteins in their extracellular matrix. Bacterial adhesion is often referred to as ‘biofouling’. Plaque on teeth or blocking of catheters can result from this effect. A concise review of the mechanisms of bacterial adhesion to biomaterial surfaces is given in Dankert (1986) and An (1998).

Polyethylene glycol (PEG) is an amphoteric material that decreases the adsorption of proteins and the adhesion of cells. PEG is used as the benchmark for comparing new antifouling materials (Dalsin, 2005; Harris, 1992). PEGylated surfaces are of interest in biomedical applications. The simplest surface modification technique, direct adsorption of PEG, leads to only weak bonding behaviour. Gombotz *et al.* (1991) used allylamine plasma glow discharge to introduce amine groups onto the surface of poly(ethylene terephthalate), which were subsequently reacted with amine-terminated PEO using cyanuric chloride chemistry. A significant reduction in the adsorption of albumin and fibrinogen was achieved, despite an incomplete surface coverage. Ratner and coworkers (Mar, 1999; Shen, 2003) have



8.10 Minimisation of unspecific protein adsorption (IgG) through different surface modifications. The measurements were carried out after a stability test using 1M NaOH for 1 h at 50°C.

demonstrated that PEG-like surfaces, which resist protein adsorption and cell adhesion, can be formed using plasma deposition of short-chained oligomers.

Figure 8.10 shows the results of minimising unspecific protein adsorption (IgG) using different surface modifications. The measurements were carried out after a stability test using 1M NaOH for 1 h at 50°C, and different plasma-based techniques were investigated. Grafting after activation with oxygen or nitrogen plasmas and plasma fixation experiments were carried out. The best results were obtained with (PEO-PPO-PEO)₂₅₀ fixed after a dip coating and with a consecutive plasma treatment.

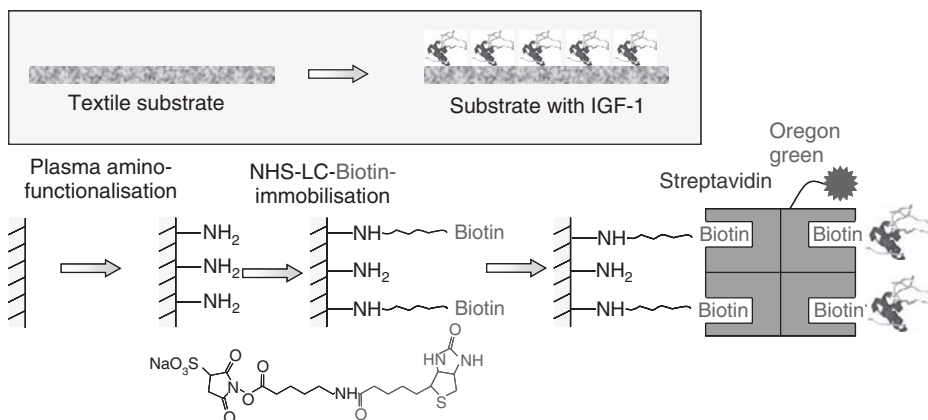
8.6.4 Example 4: Biocompatibility/immobilisation of ligand–receptor systems

Numerous biological compounds have properties of specific recognition, often referred as to ‘affinity’. Enzymatic reactions, for example, are controlled by the affinity between an enzyme and its substrate. This type of specific interaction can be used for the development of biosensors or for the specific bonding of biomolecules.

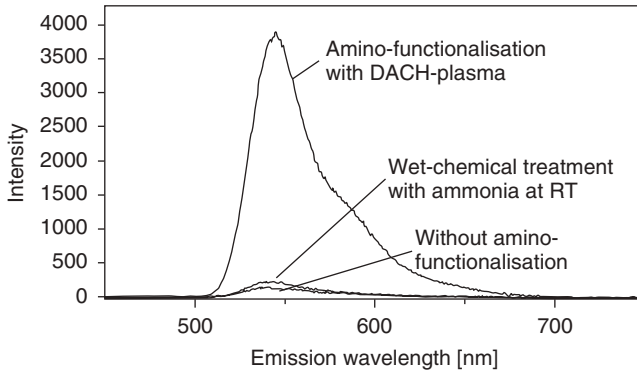
Polypeptide growth factors are powerful regulators of a variety of cellular behaviours, including cell proliferation, migration, differentiation and protein expression, and these molecules are being developed as important therapeutics in tissue regeneration, e.g. in closing bone defects and in healing chronic ulcers in the skin. The ability of immobilised growth factors to remain biologically active has been demonstrated in the very

well-characterised system of epidermal growth factor conjugated to synthetic polymer surfaces, where it was shown to be capable of directing hepatocytes to maintain their liver-specific morphology and function (Kuhl, 1996).

In collaboration with the German competence centre for biomaterials and artificial organs (BMOZ), a wound-healing non-woven pad was investigated using immobilised growth factor IGF-1, known for its support in wound healing (Ulcer). Non-wovens made of polyurethane and other substrates were used. To immobilise the growth factor, the bio-linker system biotin/streptavidin was chosen. A prerequisite for attaching biotin onto a substrate surface is the presence of free primary amino groups. Amino groups can be generated at material surfaces via plasma treatment with ammonia as the process gas. A more defined functionalisation can be obtained using allyl amine or diaminocyclohexane (DACH) with optimised plasma conditions (Müller, 1999). Figure 8.11 shows the outline of the functionalisation steps needed to immobilise the growth factor onto the non-woven material. Step 1 represents the specific functionalisation of the substrate material via plasma treatment with diaminocyclohexane as the monomer gas. The amino groups serve as anchor sites for the reaction with biotin, carried out in a wet chemical treatment step. To obtain a complete mono-molecular covering with biotin, at least two molecules should be immobilised per square nanometre. On this mono-functionalised surface, fluorescence-labelled streptavidin can be bonded onto the biotin to obtain a spacer for the biotinylated IGF-1. Figure 8.12 shows the fluorescence intensities of an untreated polyurethane non-woven compared with a



8.11 Specific bio-functionalisation. After amino functionalisation of the polyurethane non-woven via DACH-plasma treatment, NHS-LC-Biotin and consequently streptavidin were fixed onto the surface. This surface can be treated with biotinylated growth factors (e.g. IGF-1) to immobilise the bioactive species.



8.12 Fluorescence intensities measured on polyurethane non-woven after immobilisation of the fluorescence-labelled biotin/streptavidin biolinker system. An untreated non-woven is compared with amino-functionalised samples using wet-chemical treatment with ammonia at room temperature and plasma-based treatment with DACH as monomer, respectively.

wet-chemical treatment with ammonia at room temperature and a plasma-functionalised sample. The plasma treatment provides the highest amount of free amino consecutively linked with the fluorescence-labelled biolinker system. The success of the last step, the immobilisation of the growth factor, was checked with an ELISA test (enzyme-linked immunosorbent assay) (Beeh, 2000).

8.6.5 Example 5: Biocompatibility/antibacterial properties

The use of antimicrobial agents for preserving fibres and preventing the transmission of disease by materials dates back to ancient times. Linen cloth containing salt as a preservative was used by the Egyptians to wrap mummies. Ancient literature is replete with the use of silver, sulfur and other germicidal agents on clothing for health purposes. A historical review is given in Vigo (1993).

Microbial attack on textiles can be classified into two main categories. Firstly, those that are detrimental to the consumer, such as odour formation and contamination, and secondly, those that affect the fabric itself, in terms of strength reduction and quality loss. Antimicrobials are defined as agents that either kill micro-organisms (biocidal) or that inhibit their growth (biostatic). The mechanisms by which they act include:

- cell wall damage
- alteration of cell wall permeability
- inhibition of cell wall synthesis
- inhibition of protein and nucleic acid synthesis

- inhibition of enzyme action and
- inactivation of DNA.

An antimicrobial textile can act in two distinct ways – by contact and by diffusion. In the contact method, the antimicrobial agent is placed on the fibre and does not disperse, so it acts only when micro-organisms touch the fibre. In the diffusion method, the antimicrobial agent is placed on the surface or in the fibre and then migrates more or less rapidly in a humid external medium to reach the micro-organisms and inhibit their growth.

Various different agents are used to give textiles antimicrobial properties, including metals and metal salts, mostly based on silver or copper (Nakashima, 2001; Klueh, 2000); quarternary ammonium salts (Diz, 2001; Kim, 2001); N-halamines, which also enable a regeneratable finish (Eknoian, 1998); Sun, 1998); organic molecules (e.g. triclosan (Bhargava, 1996); and natural substances (e.g. chitosan (Shin, 1999) or lysozyme (Edwards, 2000)). Antibiotics may also be necessary, but, due to the possible formation of resistant strains, antibiotics should be used only for medical indications.

Fabrication methods for antimicrobial textiles can be classified into two categories, the addition of an antimicrobial agent to the polymer before extrusion (intrinsically antimicrobial fibres), or post-treatment of the fibre or fabric during the finishing stages. Plasma-based treatments can be used to create antimicrobial coatings on textiles. Chitosan can be grafted onto plasma-functionalised polymer surfaces if carboxyl groups are generated. Hun *et al.* (2001) describe the activation of PET with an oxygen plasma glow discharge treatment followed by wet chemical acrylic acid grafting and a subsequent reaction with chitosan. The poly(acrylic acid) can also be plasma polymerised on nearly all substrates using low power or pulsed plasmas (Sciarratta, 2003). A subsequent wet chemical treatment with silver nitrate produces silver carboxylated coatings, resulting in an antimicrobial finish due to the release of Ag^+ ions (Sciarratta, 2002). The silver carboxylate can also be reduced at suitable pH with mild reducing agents to obtain silver clusters at the fabric surface (Yuranova, 2003). The deposition of metallic silver can be also carried out using the magnetron sputter technique. To achieve a good adhesion of silver, low frequency (50 Hz) (Scholz, 2005) or RF (13.56 MHz) (Hegemann, 2004) plasma treatment with air or O_2/Ar -mixtures should be applied prior to magnetron sputtering.

8.7 Outlook

Plasma-based treatments are ideal for the modification of textiles due to the great variety of process types and process parameters. In the laboratory, almost all types of functionalisation of textiles can be obtained, including flame retardancy (Tsafack, 2004) antistatic finishing and self-cleaning

(Bozzi, 2005), and antibacterial finishing (Szymanowski, 2005) by applying TiO₂-layers via a plasma-enhanced CVD process. For industrial applications, improvements in machinery over the last few decades mean that several companies can now offer large-scale systems. Nevertheless, the systems are mainly used to increase hydrophilicity (for wettability, dye-uptake and printability), because this process is easier to handle and air can be used as the process gas. For hydrophilisation, atmospheric-pressure plasma treatment is the method of choice because the finishing can be done roll-to-roll. For special coatings that require plasma polymerisation, commercial applications are still unavailable, due to the more complicated process, longer process times and higher production costs. Another problem is the fact that plasma polymerisation also coats the electrodes and the inner walls of the system components, so the equipment must be cleaned regularly to avoid alterations in the plasma parameters and therefore a change in the properties. But new demands for technical textiles will drive continuing developments in plasma-based techniques due to the outstanding possibilities for finishing material surfaces without alteration of their bulk properties. Plasma-based treatments of fibres and yarns, important to avoid the shadowing effects which can occur during fabric treatment, will be improved to overcome slow treatment speeds and make them available for commercial applications.

8.8 References

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