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White paper on the future of plasma science and technology in plastics and textiles

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:
Cvelbar, U., Walsh, J.L., Černák, M., de Vries, H.W., Reuter, S., Belmonte, T., et al. (2019). White paper on the future of plasma science and technology in plastics and textiles. PLASMA PROCESSES AND POLYMERS, 16(1), 1-37 [10.1002/ppap.201700228].

Availability:
This version is available at: https://hdl.handle.net/11585/674300 since: 2019-02-26

Published:
DOI: http://doi.org/10.1002/ppap.201700228

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(Article begins on next page)

12 October 2024

This is the final peer-reviewed accepted manuscript of:

Cvelbar, U. et al. **White paper on the future of plasma science and technology in plastics and textiles**

in

PLASMA PROCESSES AND POLYMERS Vol.: 16 Issue: 1,SI Article N.: e1700228, 2019.

The final published version is available online at: https://doi.org/10.1002/ppap.201700238

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White paper on

The Future of Plasma Science and Technology in Plastics and Textiles

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Keywords: Plasma, Plastics, Textile, Trends, White paper

Abstract

This white paper considers the future of plasma science and technology related to the manufacture and modification of plastics and textiles, summarizing existing efforts and the current state-of-art for major topics related to plasma processing techniques. It draws on the frontier of plasma technologies in order to see beyond and identify the grand challenges which we face in the following five to ten years. To progress and move the frontier forward, the paper highlights the major enabling technologies and topics related to the design of surfaces, coatings and materials with non-equilibrium plasmas. The aim is to progress the field of plastics and textile production using advanced plasma processing as the key enabling technology which is environmentally friendly, cost-efficient, and offers high-speed processing.

Introduction

Plasma as a source for the activation of surfaces and materials or their oxidation has been on the technological frontier since the first humans learned how to produce sparks and light fire. Of course humanity has moved a long way from simply creating fire, or generating so-called thermal plasma for cooking purposes. In today's world, which has seen tremendous scientific and technological progress over the last 100 years, perhaps the greatest achievement of plasma science is its application in the microelectronics manufacturing sector. This becomes obvious, when looking at the fact that everyone carries a mobile phone, has a personal computer or watches TV. It is almost impossible to imagine any microchip fabrication without the use of thermally non-equilibrium plasmas generated at low-pressures, which are an excellent tool that provides a processing environment where atom-by-atom

manipulation is possible. Slowly plasma technology has moved forward over the last two decades into every pore of our daily life.

Plastics and textiles are present in our everyday life from morning until evening, when we wake up and dress, go shopping from bags to food packaging, driving a car, sitting on the chair, etc. When we reflect back over the past day, then the question that poses itself is how plasma can contribute to societal challenges and improve plastics and textiles. Plasma, as a processing tool, can contribute to challenges in health related issues connected to medical and/or smart textiles and polymers, food security, energy related subjects, fuel cell membranes, solar cells and flexible electronics. One of the biggest benefits is related to the environment, where safe and ecologically benign plasma processes will contribute significantly to the preservation of today's world by replacing existing chemical processes, and moreover they will enable biodegradable and light-weight material preparation and processing.

Figure 1. The schematic representation of the today's world rotating around plasma processing and plastics & textiles. Courtesy of Malte von Tiesenhausen, Visual Facilitators and INP Greifswald.

Topics that we deal with when discussing the use and application of plasma technology for improving the properties of plastics and textiles are linked to the type of plasma to be used, monitoring of plasma parameters to control plasma at the atomic level, understanding of the interactions of plasma with polymers/textiles, developing new plasma sources and systems, substrate properties, aging of surfaces

and materials, development of coatings, scaling up the technologies for large scale treatments, the relationships of costs-efficiency-stability of treatments, etc. A simple response to "why use plasma for plastic and textiles processing?" is that plasma is a dry treatment and green technology that enables nano-atomic scale modifications of materials. The plasma discharge generated in gas provides dry treatment of surfaces, where no drying process is required. It is a green technology, where there is little need for the use of hazardous chemicals, thus it produces little waste and presents a significantly reduced ecological load to environment, whilst simultaneously enabling the same, if not even better, processing efficacy. Furthermore, it offers additional flexibility through various plasma chemical approaches, where both gas/liquid systems are supported for the treatment of any solid, fiber or polymer material. It offers possibilities ranging from single atom manipulation, targeted molecule incorporation, selective polymer bond breaking to other nanoscale modifications with exceptional precision. Competing technologies to plasma processing include wet chemical technologies with environmental issues, laser treatments with limited penetration depths, slow photo-chemistry and, in some cases, chemical vapour deposition or flame treatment and deposition.

High speed, low cost products	*Higher value, lower throughput products*
Packaging Barrier layers, anti-diffusion layers, active packaging – indicating, display, etc.	**Flexible optoelectronics** Semiconductors, conductors, insulators, optical layers on polymers, barrier layers for environmental protection nanostructures, plasmonic structures
Renewable polymer materials Paper based coatings, natural polymer, coatings and treatments, controlled biodegradability, fibre and textile treatments	**Biological polymers and textiles** Anti-bacterial, biocompatible, cell-friendly
Textiles Active, functional textiles (e.g. built-in sensors), etc.	

Figure 2. Product classes based on the cost and production scale.

The application of plasma technology for plastics and textiles processing can be divided into classes based on the ultimate value of the product (Figure 2). Industrial plasma processing at very high speeds with good reliability is always a goal but is not always achievable as a balance must be struck between cost and performance. In the packaging sector, material throughput and processing performance are key factors. Plasma can be used for the disinfection of products, deposition of barrier layers, anti-diffusion layers, adhesion of dye or colour, adsorption and dispersion of liquids. In the same category, we can also find renewable polymer materials, such as paper based coatings, natural polymers, textiles, fibers, which require surface functionalization for improved adsorption or bonding as well as deposition. Similarly some textiles require comparable processing techniques in order to achieve proper activity and functionality. On the other side of spectrum are high end products, where lower throughput is more than satisfactory, but at much higher precision. In this class, we find most of the electronics based on polymers, like flexible and optoelectronics, semiconductors, conductors, insulators, barrier layers for protection, nanostructures, plasmonic structures as well as biological polymers and textiles which are antibacterial and biocompatible.

When the frontiers of plasma science and technology for processing are projected, three major pillars carry the weight of the future grand challenges in the field with an additional pillar that should be constructed over the next ten years. The pillars with detailed tasks are presented schematically in Figure 3. The *future grand challenges of plastic and textiles* are:

1. *Developing enabling technology for plasma sources and processes*;
2. *Design of smart surfaces on polymers and textiles*;
3. *Design of complex surface coatings including those with macromolecules and nanomaterials*;
4. *Design of new advanced materials and structures (to be constructed).*

The key to upgrading and moving the plasma processing frontier forward is to develop new enabling technologies for the field, which will provide grounds for the design of smart surfaces and complex coatings. Furthermore, in the forthcoming years we might see the rise of a new pillar where plasmas will become a tool for the design of completely new advanced materials and structures such as self-repairing materials.

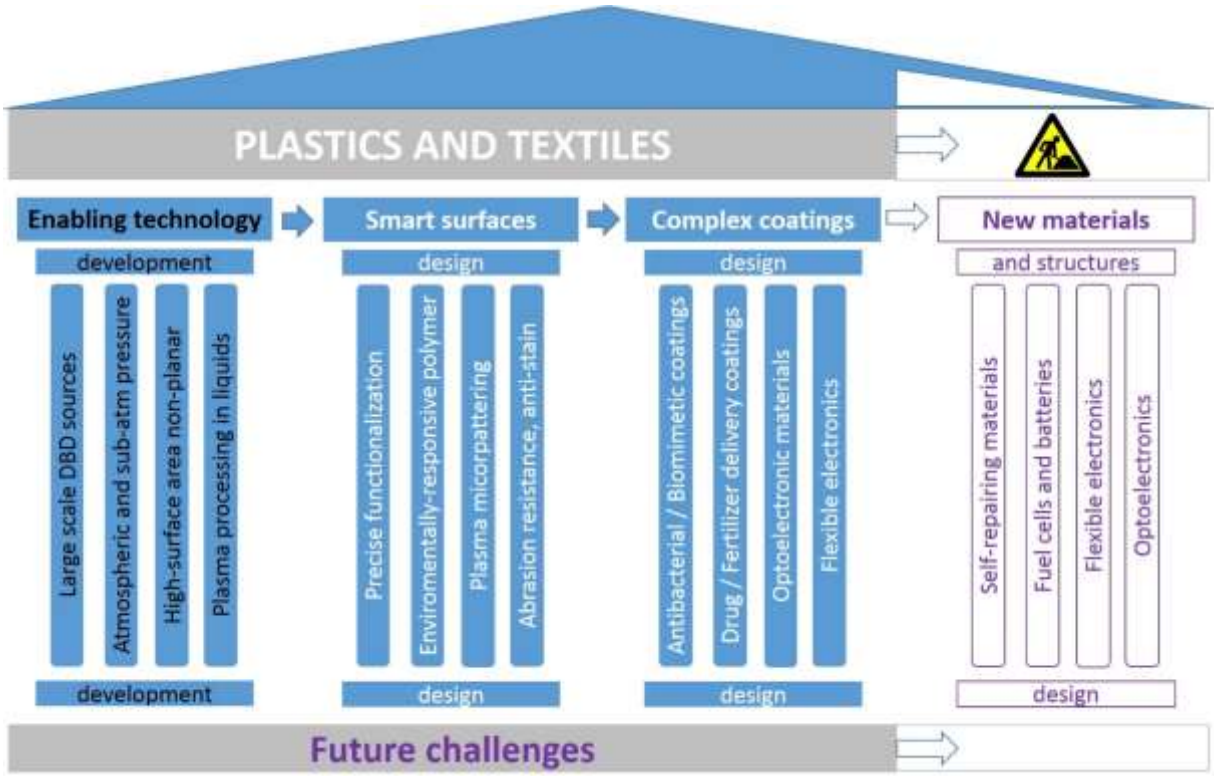

Figure 3. Building the future with major pillars of plasma science and technology for plastics and textiles field.

In this paper, the three major challenges are systematically divided into sub-challenges (as presented in Figure 3), where the current state-of-the art is described in detail along the future vision and set directions.

1. Developing enabling technology for plasma sources and processes

1.1 Large scale DBD plasma sources

Atmospheric pressure Dielectric Barrier Discharges (DBD) have been under active investigation for well over a century and are the tool of choice for a wide variety of industrial processes; examples include large scale ozone generation, odour removal and materials processing. Of all the techniques capable of sustaining a non-thermal discharge under high pressure conditions the DBD is perhaps one of the most convenient due to its ease of scalability and relative stability. [1] In the context of industrial scale

materials processing, DBD plasma systems are able to satisfy many of the key requirements, including: (1) large-area treatment, (2) high-throughput, (3) treatment uniformity, (4) system reliability and (5) energy efficiency.[2] Due to these beneficial characteristics, the replacement of conventional materials processing methods, such as vacuum-based or wet chemical approaches, with DBD based techniques is an area of intensive research. While atmospheric pressure DBD's are widely used for surface modification and activation on an industrial scale, it is only recently that their potential for the deposition of thin films and functional coatings has been explored.

Recent research and development activities exploring DBD based materials processing techniques have focused on the power source and electrode design to enhance both the electrical efficiency and discharge uniformity. Many large area plasma processing systems employ electrical power sources that operate in the Hz to kHz frequency ranges at power levels well in excess of 10 kW.[3] Low frequency operation, especially at line frequencies (50 – 60 Hz), greatly simplify the design of the power source, yet can compromise the plasma generation efficiency and uniformity. DBD systems operating in the kHz frequency range tend to employ solid state switched mode power convertors using high power semiconductor switching devices (e.g. IGBTs) combined with a resonant output transformer.[4] Such systems offer excellent reliability and high efficiency, whilst the higher frequency of operation promotes the uniformity of the discharge and enhances the density of plasma generated reactive species.[5] As researchers strive for even higher frequency operation (e.g. >100 kHz), many power semiconductor devices become inefficient due to their long switching times, hence power MOSFET's are one of the few choices available to the power source developer. In terms of electrode design, roll-to-roll processing systems that incorporate a DBD discharge are widespread.[6] The characteristics of the DBD make it highly amenable for application in roll-to-roll processing, especially where the material to be treated forms part of the dielectric barrier, as in the case of polymer treatment.

Despite the widespread usage of the DBD configuration in materials processing applications, several challenges still remain. A drive to increase material throughput necessitates the use of large area discharges; this has the potential to place an undue burden on the plasma power source. Large area electrodes operating with a narrow gap separation and a high permittivity barrier material yield a large electrode capacitance. Under high frequency excitation a significant displacement current can flow, stressing the power source and reducing the electrical efficiency of the system. Much recent research has focused on the use of advanced excitation techniques, such as nanosecond pulsed or radio-frequency excitation, to improve the uniformity of the discharge.[7] While such techniques hold much promise, their implementation for DBD generation on an industrial scale is challenging due to the extreme requirements placed on the power source arising because of the large area electrodes.

For many materials processing applications the potential for a DBD to operate in a filamentary mode can pose a considerable challenge; filaments tend to result in localised high-temperatures that can damage thermally liable substrates. For applications employing DBD systems to deposit high-quality coatings, the spatial non-uniformity of the discharge can potentially lead to a non-uniform coating; however, recent results have shown that filamentary DBDs are able to deposit films with very smooth morphologies under carefully controlled conditions.[8] Through the recent development of advanced plasma power sources and gas delivery systems, highly uniform atmospheric pressure DBD's can be realised in a variety of electrode geometries and complex gas mixtures.[9] Such efforts have led to the successful demonstration of pilot-scale roll-to-roll DBD deposition systems operating under ambient conditions; see Figure 4 for example, which shows a prototype roll-to-roll DBD system developed by Fujifilm, TU Eindhoven and Differ. The system is capable of generating a uniform discharge in a variety of gases including air and has proven effective for the deposition of ultra-smooth organo-silicone layers and carbon free silica like layers with excellent barrier properties.[9b, 10]

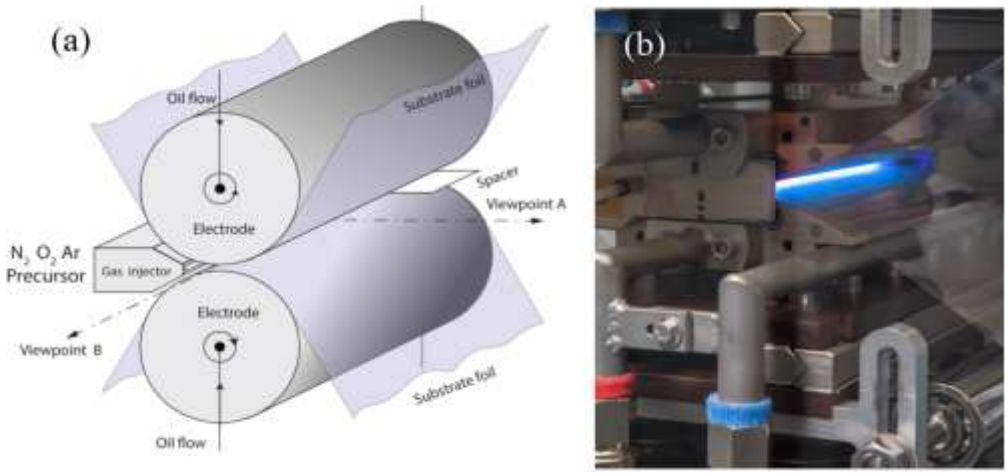

Figure 4. (a) Schematic of prototype roll-to-roll DBD system. (b) Photograph showing discharge generated during polymer film treatment. (Photo courtesy of M. v.d. Kerkhof, Fujifilm BV, NL)

One alternative approach employed by several researchers is to generate a discharge that can be physically decoupled from the sample under treatment. The use of Diffuse Coplanar Surface Barrier Discharges (DCSBD) circumvents issues related to discharge non-uniformity as the treated sample can be placed in close proximity to the discharge and thus receive a considerable flux of reactive species without being exposed to filaments should they arise. Figure 5 shows a commercial DCSBD source producing 0.5 m^2 of air plasma at the power density of some 100 W/cm^3.[11] The source produces a 0.3 mm discharge layer on the dielectric surface and can be used for the direct treatment of materials, including typical textiles and porous materials which are immersed directly in the plasma;[12] or, for the remote treatment of materials, such as polymeric or metallic films that are placed a few mm from the discharge.

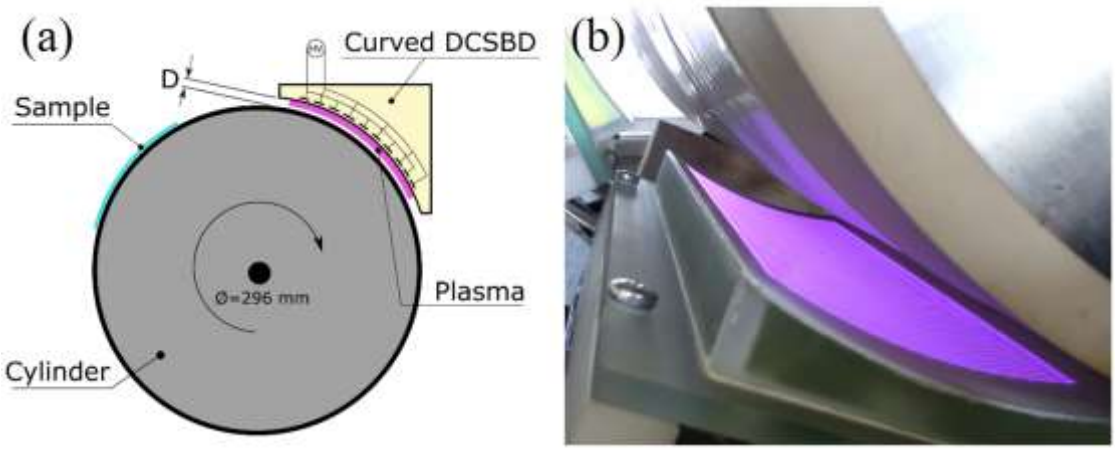

Figure 5. (a) Schematic of roll-to-roll Diffuse Coplanar Surface Barrier Discharge reactor. (b) Photograph showing remote treatment of thin film material.

Looking forward, our understanding of the underlying physical and chemical processes within the DBD is rapidly evolving due to the availability of advanced plasma diagnostic techniques[13] combined with

multiscale, multiphysics and multidimensional plasma modelling.[14] Despite this excellent progress, many aspects relating to the interaction between the multitude of plasma generated species and the surface and how this interaction influences the discharge dynamics remain poorly understood.[15] Uncovering a deeper insight in to these complex processes is vital to guide the future development of plasma power sources that are able to elicit desirable plasma-surface interactions. The use of non-conventional plasma power sources for materials processing, such as short-duration pulsed excitation, has already shown benefits over more conventional techniques. Recent examples include the use of dual frequency excitation, combining both MHz and kHz excitation, and the use of nanosecond pulsed excitation with both techniques offer the exciting possibility of manipulating the energy of electrons within the discharge, providing a level of control over the electron dynamics that is currently beyond our reach. As our understanding of the fundamental processes continues to grow, it is likely that these advanced plasma power sources will see greater industrial implementation. To supplement the future development of sophisticated plasma power sources, further efforts should be devoted towards the development of *in-situ* plasma monitoring and diagnostics approaches. Establishing a feedback mechanism to convey the discharge characteristics back to the power source in real-time is critical to ensure the consistency of the process.

It is anticipated that as DBD technology evolves, further industrial materials processing applications will migrate from a batch processing approach conducted under vacuum conditions to a continuous processing approach under atmospheric pressure conditions. This would be a major breakthrough for many applications, especially those involving material deposition. Advanced DBD technology is easily integrated with other roll-to-roll (wet) coating steps, facilitating the high volume processing of advance functional coatings (organic and inorganic) for applications in the field of flexible electronics, barrier films (from packaging, thin film photovoltaics (PV) to organic led emission display (OLED) encapsulation) and membranes.

1.2 Atmospheric and sub-atmospheric pressure discharges

Over the last decade, as already described before, dramatic evolutions were brought to plasma sources operated near, or at, atmospheric pressure. One way to differentiate atmospheric pressure plasma sources is to separate them between 1D and 2D discharges. In the field of textiles, it is possible to treat either raw materials such as yarns, or woven products such as fabrics or cloths. The issue of what is treated is closely related to the modification brought by the treatment. The need for increasingly sophisticated materials has to be considered prior to any plasma source design. Indeed, we readily understand that if a composite material is foreseen to create, e.g. a fire-resistant stretchy fabric, it will be necessary to determine how flame-retardant charges have to be incorporated into or deposited onto the yarn without stiffening the assembly.

Typically, plasma processing can be considered as a surface functionalization technique. Plasma processes determine the properties of the finished polymer or textile product.[16] However, the bulk material properties are kept constant, under condition that the materials are thick enough. Modification of surface properties by plasma are achieved: i) by polymer etching and functionalization[17] with the use of a precursor gas that does not polymerize such as argon, hydrogen, nitrogen, carbon dioxide, but also oxygen;[18] ii) by deposition of a polymer or inorganic thin film; iii) by a two-step polymerization process, where in the first step, the surface is activated by plasma and in the second step, a precursor is added; and iv) finally by simultaneous activation and plasma polymerization of the component. However, when materials become thinner and thinner (around several µm), the bulk properties (such as tensile strength) might be affected by plasma processing.

Plasma technology has been used for treating fibres and/or fabrics for about 40 years. Nowadays it is strongly anchored within specific industrial sectors such as paints, coatings and microelectronics.[17, 19]

Among the DBD sources, the possibility of continuously treating yarns or wires appeared recently with the tubular dielectric barrier discharge.[20] Such a device is designed to let the wire come in and get out of the reactor without contact with the surrounding air, thanks to a gas curtain. If deposition rates are about 1-10 $nm \cdot m \cdot s^{-1}$, an increase by at least two orders of magnitude is required at the industrial scale, which is quite conceivable. To go a step further, PECVD of composite coatings can be achieved with an additional source of aerosols that convey nanoparticles to the plasma region. Although, the concept of double-frequency discharges is not new, their use at atmospheric pressure in pulsed DBDs is an elegant solution to incorporate nanoparticles into a plasma-polymer matrix.[21] Indeed, by mixing a low-frequency signal (hundreds of Hz) to drive the nanoparticles to the substrate with a high-frequency (thousands of Hz) signal to trap them in the plasma, it is possible to achieve significant and spatially uniform deposition of nanoparticles across the substrate surface. The use of an aerosol is however difficult, as nanoparticles tend to agglomerate at the liquid-gas interface of the evaporating droplet. Another way to manage nanoparticle introduction is to produce them *in situ*. To get a quasi-monodisperse distribution of chemically-controlled nanoparticle with mean diameters of below 3 nm typically, electrode vaporization in DBDs is the most convincing way.[22] However, nanoparticle production yields are rather low (~10^{-12} mol J^{-1} at the lab scale), even though the mass production rate depends on the input power related to the product of the energy controlling the production per filament times the number of filaments per second. Atmospheric-pressure dielectric barrier discharge with capillary injection for gas-phase nanoparticle synthesis has been proposed to obtain narrow size distributions at higher rates. The main idea is to control the residence time of a given precursor in a DBD by controlling its injection via a capillary to create a jet effect.[23] Recently, a micro hollow cathode plasma jet was used to generate copper containing films on an ABS substrate. The high temperature, of around 1500°C, is quickly quenched by the high gas flow so that room temperature was reached at a distance of 1 cm.[24] A careful balance between etching and deposition during the plasma process allows the generation of nanostructured coatings on yarns and textiles.[25]

The idea of using thermal plasmas (*e.g.* blown arcs) as localized sources for coatings enables the formation of extremely porous, yet non-powdery, coatings.[26] By injecting high energy into discharges located very near substrates moving past the source at high speed makes it possible to transfer a part of this energy to surface chemistry without damaging the substrate. The main difficulty to deal with is the delicate arrangement of the source with respect to the moving substrate. This aspect can be partly overcome by resorting to afterglows, at the expense of the reactivity.[27] Contrary to blown arcs, electrode-less system such as radiofrequency or microwave torches can be used to avoid the presence of metals from electrodes as trace elements.[28] Operated at sub-atmospheric pressures, DC discharge jets can be run supersonic so that active species are 'spray-deposited' onto the surface of interest with different morphologies (nanoparticles, dense columnar films, or hierarchical nanostructures, etc.). [29] In contrast, resorting to nanosecond-pulsed plasmas paves the way for highly-controllable plasma polymer deposition and surface functionalization at room temperature.[30]

If open-air technologies are widely spread, the need for well-controlled atmospheres will be more prevalent in the years to come. Impurities at concentrations as low as 10 ppm are known to considerably affect the discharge behaviour. Removing oxygen and water is usually a hard task in continuous-flow processes.[31] Gas curtain technologies should be preferred to sub-atmospheric pressure reactors if the treatment cost does not exceed a few percent of the value of the treated substrate. Otherwise, differentially-pumped stage units are required, which notably increases the overall expense needed to set up and sustain a process. A further alternative to a controlled

environment is the use of liquid precursors such as those used by Dow Corning Plasma Solutions (DBD based process) and Ahlbrandt Systems GmbH (Corona based process).[32] Also classical sol-gel processes can benefit from a plasma treatment prior to the depositing process step.[33]

The trend towards the use of cold non-equilibrium plasma processes at higher pressure allows for a cost-efficient manufacturing line. However, process monitoring is much more difficult than for the case of low-pressure plasma processes. Small scales, collisionality and non-equilibrium plasma chemistry obscure standard diagnostic techniques such as quantitative optical emission spectroscopy, Langmuir probe methods or mass-spectrometric plasma monitors. Complex diagnostics exceed the cost limit and increase maintenance dramatically. Here, reliable methods at atmospheric pressure such as absorption spectroscopy[34] need to be implemented for a reliable, fast and cost efficient process monitoring.

Molecular feed gases in jet-like non-equilibrium plasmas lead to filamentation and consequently result in inhomogeneous deposition. The use of noble gases – especially helium – generates homogeneous plasmas at high pressure. Furthermore, highly energetic metastable noble gas species will strongly influence reaction pathways. For large-scale deposition processes, noble gas plasmas are not suitable, due to the high cost of the feed gases. Promoting the lowest gas consumption in novel plasma sources will open the market for large-scale polymer and textile deposition using noble gas based plasmas with a better control over the deposition process and more homogeneous deposition.

Another important and still open issue of atmospheric and sub-atmospheric pressure sources is their capability of homogeneously treating three-dimensional substrates, *i.e.* porous materials, patterned surfaces or topologically-complex objects.[35] Two strategies to tackle this include developing high-voltage (tens of kV) nanosecond pulsed sources operating at high frequency (tens to hundreds of kHz) on the one hand and gradient-limited sources mounted on a robotic arm on the other hand. This trend is usually accompanied by the need to reduce both the duration and energy consumption for continuous plasma processing.

Current trends in plasma technology development are the combination of multiple techniques both plasma based and non-plasma based. In low-pressure deposition, the use of magnetron sputtering in combination with glow discharges allows a tailoring of thin film properties. Also at atmospheric pressure, synergetic effects can lead to a more controlled deposition process.

1.3 Dealing with larger surface areas of non-planar substrates

Plasma treatment of complex-shaped surfaces due to porosity, roughness and micro-texture is more challenging than coating or etching flat substrates. In fact, fabrics can show large surface areas, one order of magnitude higher than flat films. [25, 36] The main objectives for an efficient plasma treatment of a non-planar surface are, in priority of order: (1) uniform coating, (2) acceptable film properties or surface finishing, and (3) high deposition rates. The achievement of these objectives requires reaching milestones concerning film quality, process reproducibility, economical and ecologically-friendly aspects. This section addresses these issues with the aimofsummarizing the state of the art in plasma treatment of 3D plastic objects and textiles, while drawing attention to the main challenges envisaged in this research field for the next few years.

The first question to start with is: atmospheric or low-pressure plasma? [36] Currently, the plasma coating industry is dominated by magnetron sputtering and plasma-enhanced chemical vapour deposition (PECVD). [37] Both methods involve discharges held at pressures ranging from 0.1 to some tens of Pascal. The cost of maintaining the required vacuum in such plasma chambers is one important

drawback. On the contrary, the a-priori more cost-effective atmospheric plasma processes must be conducted with restrictions such as small interelectrode distances and relatively large gas flow rates. Dielectric barrier discharges (DBD), as well as corona discharges, have found their application in coating micro- and nano-structured objects such as textiles on planar electrodes.[36] However, the samples are composed of individual fibres, whose arrangement usually diminishes plasma uniformity due to the formation of streamers. Atmospheric pressure plasma jets (APPJ) are milder than plasma touches and excellent resources for treating 3D substrates, for example macroscopic plastic objects.[38]

At low pressures we can highlight the inner coating of plastic bottles and packages with gas barrier layers such as SiOx thin films by means of a microwave Plasmaline antenna (Figure 6a).[39] Variation of deposition parameters such as substrate bias enables enhanced barrier film properties, i.e. reduce oxygen transmission rate (OTR) (Figure 6b). The current trend consists in reducing as much as possible the density of coating defects in order to preserve the functionality of the gas barrier film. One expects reaching a density of defects low enough to attain a barrier improvement factor (BIF) of at least 150. BIF is defined as OTR_{polym} divided by OTR_{coat}. The coating defects are visualized by means of scanning electron microscopy (SEM) after a treatment with oxygen plasma which localizes the defect positions. Less than 200 defects·mm^{-2} have been achieved; however, it is necessary to reduce this to well below 100 defects·mm^{-2} in order to reduce substantially OTR.

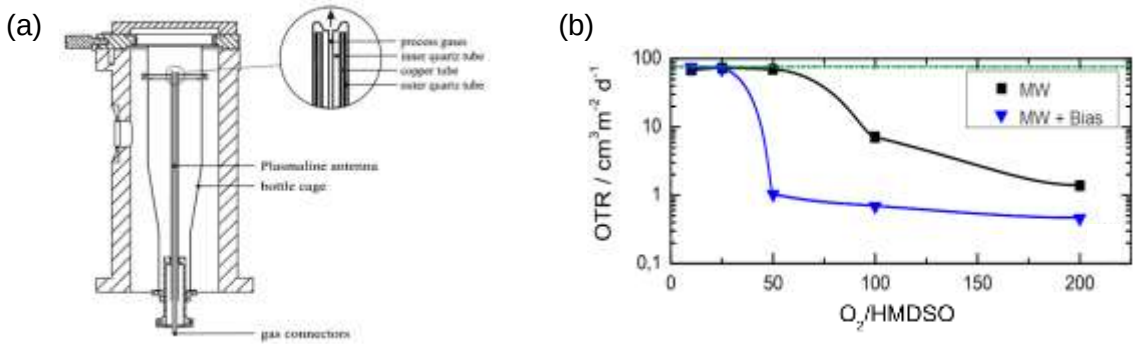

Figure 6. (a) Schematic of the reactor system for gas barrier layer deposition on the inner surface of a PET bottle. Height and diameter of vacuum vessel are 400 mm and 140 mm, respectively. Diameter of bottle cage is 85 mm, and diameter of the microwave Plasmaline antenna (inset) is 12 mm. Reprinted from ref.[39a], with permission from Wiley. (b) OTR of coated PET foils as function of O_2/HMDSO ratio with a substrate bias of 36 V (MW + bias) and grounded substrate holder (MW). PET foil OTR reference is indicated as dashed line. Image extracted from ref.[39c]

High power impulse magnetron sputtering (HiPIMS) discharges provide coatings with superior properties thanks to the efficient ionization of sputtered metal atoms (Figure 7a).[40] Hence, the discharge enters into the metallic plasma regime. Uniform coatings of metals or ceramics showing complex-shaped structures constitute another highlight of HiPIMS (Figure 7b).[40b, 41] Not only sharp edges of cutting tools can be homogenously coated, but also textiles due to a larger penetration depth of the discharge. For example, silver deposition on fabrics has been successful in the inactivation of bacteria thanks to the very homogeneous film deposition (Figure 7c).[42] Dense coating within micrometer ranged trenches has been achieved [40a, 43] and the next step consists in lowering the minimal pitch size to the nanometer range.

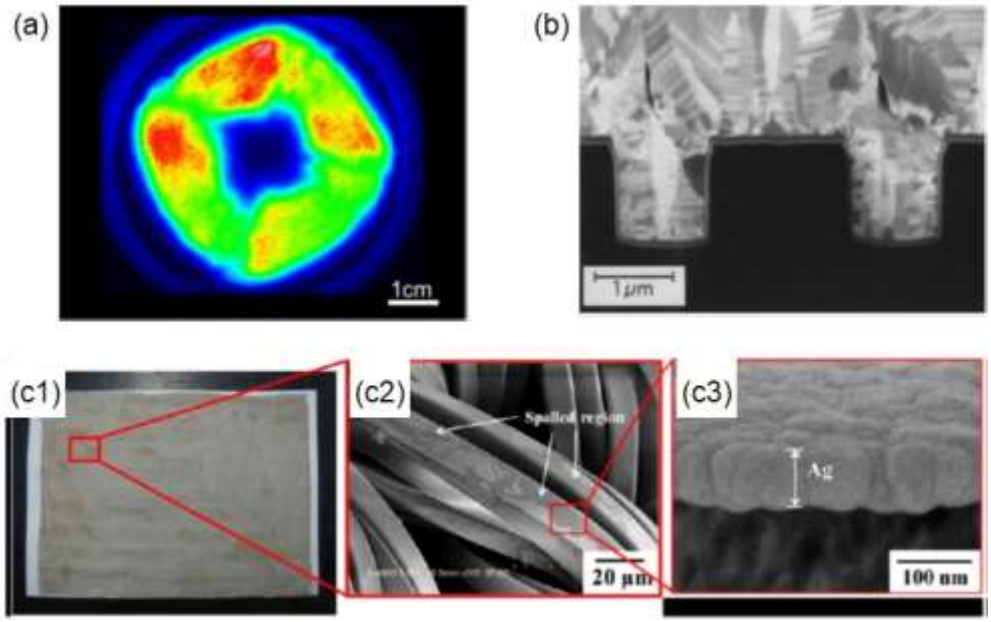

Figure 7. (a) Front-view of the racetrack of a HiPIMS target showing the optical emission of plasma species. Reprinted from ref.[44] with permission from AIP Publishing. (b) Cross section SEM images of two via holes homogeneously filled by Cu using HiPIMS. Reprinted from ref.[40a], with permission from Elsevier. (c) Different magnifications of washed PET fabric with HiPIMS-deposited silver coating.[42b] (published under a Creative Commons license: https://creativecommons.org/licenses/by-nc-sa/3.0/)

In fact, HiPIMS is a very appropriate technique to treat textiles, but a few issues are unresolved. A known drawback of this technique relies on the relatively lower deposition rates compared to DC magnetron sputtering. One solution consists of performing hybrid DC+HiPIMS plasma deposition, where the deposition rate can be parameterized with driven HiPIMS power fraction.[45] A future challenge consists of overcoming the deposition rates of conventional DC sputtering. Another issue in HiPIMS is the instability in the form of rotating plasma spokes (Figure 7a).[44] It is necessary to investigate their formation and properties in order to understand the process of film growth/etching. Optimization of HiPIMS plasma processes can be carried out by means of systematic variations of technological parameters, as for example pressure, residence time and pulse frequency.[37]

Direct plasma exposure can be detrimental for the structure and composition of polymers, so different tactics such as remote plasma[43] and deposition of a thin initial layer that is re-sputtered and ion bombarded have been considered. Another relevant issue for polymeric samples is surface charging. Recently, simulation efforts towards surface charging phenomena on rough polymer surfaces have been performed.[46] This study identifies the expected screening potentials (ca. 50 V) developed on high surface area polymer surfaces affecting ion energy distributions and etching rates. Further efforts in the understanding of plasma-polymer interactions comprise modelling of elementary surface modifications by in-situ diagnostics of the chemical state[47] and by real-time control of the optical properties of the polymer top layer.[48] The synergistic effect of UV radiation and ion bombardment have been addressed in numerous studies and a key point in the future will be to understand the isolated effects of photons and ions on polymers.[49]

1.4 Processing of materials by plasma in liquids

Plasma in liquid has recently attracted considerable attention from researchers in the field of synthesis and structural modification of materials. Such interest is explained by the obvious potential of plasma technology for producing many valuable gas and solid-phase products. The generation of plasma in liquids with nanosecond and microsecond voltage pulses for material modification is very new, but the approach offers great potential to be highly flexible with regard to the range of applications. This is very important if we would like to make the plasma approach for a viable replacement for wet chemical processing. The synthesis of nanomaterials and structural modification of polymer membranes by plasma in liquid has been mostly developed after 2005 and the interest is growing mainly due to the simplicity of the experimental design, eco-friendliness, and one-step approach.[50] When water is subjected to a gaseous discharge, a high number of gaseous excited species, such as hydrogen, oxygen, nitrogen, and hydroxyl radicals are produced, which then may efficiently interact with water molecules as well as bulk materials, inducing structural modifications.[51] Furthermore, methods using plasma in liquid offer a number of additional capabilities.[52] Liquid plasma-assisted functionalisation is faster than solution chemistry and is a one-step approach. Tailoring the material surface with different functionalities is also possible, due to a wide range of functional groups that can be generated by plasma in liquid through the use of combinations of solvents and solutes in solutions. One of the main advantages of the application of plasma in liquid is that reactive species can be produced cost-effectively at low temperatures and *in-situ* without the need for storage or the necessity of disposal of environmentally hazardous substances. Generation of discharges in or above liquid is based on a range of electrode configurations and voltage regimes as well as on the possibility of using different liquids of different polarity.

Plasma in liquid systems can be subdivided into four main groups, depending on the electrode material, configuration, liquid type and power source:[53] (1) gas discharge between an electrode and the electrolyte surface (in contact with the liquid), (2) direct discharge between two electrodes immersed in liquid, (3) contact discharge between an electrode and the surface of surrounding electrolyte and (4) radiofrequency (RF) and microwave (MW) generation.

The key advantage of using plasma in liquid, in contrast to conventional solution based methods, is the production of reducing agents. In the plasma, not only are free electrons and ions with certain energies, dependent on the discharge mode formed, but also radicals which may cause physical and chemical reactions in the plasma-liquid interface and in the liquid (Figure 8). For example, the case of nanomaterial formation can be attributed to reduction, oxidation, and sputtering. Reducing species produced by the plasma in a liquid have different lifetimes and different reducing abilities. Adjusting the reducing species by tuning the plasma parameters enables the synthesis process to be controlled not only from the solution phase as in a usual solution-based synthesis, but from the plasma phase.[53-54] The diversity of reducing species formed in plasma increases the complexity of analysing the synthesis mechanisms, but also offers the possibility of controlling the type and structural properties of the nanomaterials by adjusting plasma parameters.

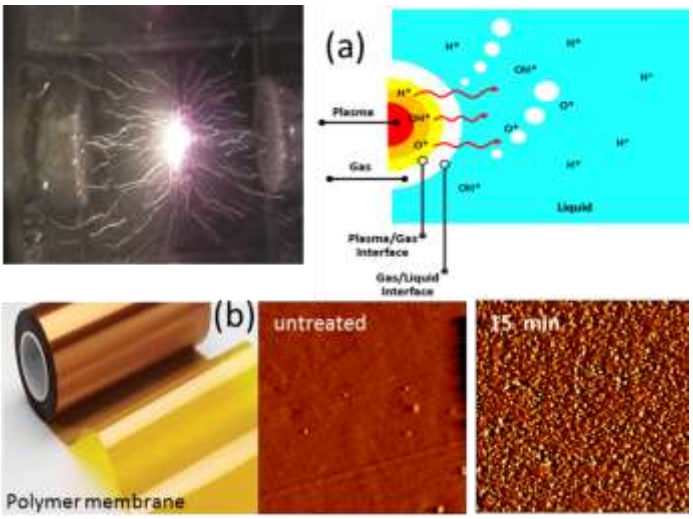

Figure 8. (a) Plasma discharges in liquids generated in liquids between electrodes arranged in a rod-to-rod configuration. (b) AFM measurements of polymer membrane treated by plasma in liquids.

Recent studies have also demonstrated the utility of plasma in liquid techniques for the surface modification of polymer films and membranes.[50e, 55] Improving the adhesive properties of polyester cord threads used for reinforcing materials.[55a, 55b] Moreover, textiles treated in water solutions containing silver ions become antibacterial due to reduced silver atoms on the textile surface.[55b] A permanent surface hydrophilization of outer and inner surfaces polytetrafluoroethylene tubes used in the biomedical field was achieved by subjecting these materials to plasma generated in liquids.[55c] Polyimide films usually used in the microelectronics industry have shown an increased surface hydrophobicity and changes in electrical properties after treatment by plasma formed in water.[50d, 50e] Also, significant changes in some intrinsic fluorescence features, such as the intensity and the position of the emission peaks, have been observed during exposure to plasma-activated water. Chemically active species and shock waves are formed in the discharge which may interact with molecules and bulk-materials, inducing surface and bulk modification. These excited species do not induce drastic structural modifications in materials because they are quenched by the liquid in which the discharge is generated. Preliminary experiments using nanosecond voltage pulses (10 ns) showed that structural modifications achieved for polyimides that differ significantly from treatments with plasmas in liquid that have been generated with longer high voltage pulses (50 µs).[50d, 50e] When using nanosecond voltage pulses, a topographical rearrangement of the polymeric chains is predominantly induced within the bulk structure, while more intense surface modifications dominate when microsecond pulsed discharges are employed to treat the polymer films. A deeper understanding of the liquid-phase plasma is needed for the control of the surface and bulk materials interactions that can be promoted this way.

Plasma-liquid systems can be framed within highly important and contemporary plasma research. This research is strongly interdisciplinary and offers many future challenges. For this reason, new applications are rapidly emerging even though this field is only in its infancy. The tailoring of plasma parameters allows us to control the yields of different reducing species or the velocity of generated shock waves, controlling then the final size and shape of nanomaterials, or the type of functional groups for polymer films surface decoration. Although many achievements in the area of plasma in liquid for the synthesis and surface modification of materials have been already realized, the spatial and temporal evolutions of detailed processes that occur at the plasma-liquid interface, in the bulk plasma, and in the liquid, are still not well understood. Plasma in liquid is a highly non-equilibrium state due to the fact that the plasma can be generated in both liquid and gas (bubbles) states. An important issue is to stabilize and control them. Due to the finite resistivity of polar liquids, charging of the energy

storage must always be pulsed.[55d] After uncovering the detailed processes, the specific reactions in the plasma may be tuned by changing the corresponding parameters, and finally materials processing with desirable properties can be achieved.

2. Design of smart surfaces on polymers and textiles

2.1 Precise functionalization for improved bonding

One of the oldest and most frequent uses of plasma in the design of polymers and textiles is plasma functionalization of surfaces with the aim of improved bonding.[56] In this process, plasma creates certain functional groups on the surface of the polymer as well as breaks bonds. These sites become populated by targeted functional groups that are either created by the plasma, depending on plasma type, or by grafted functional groups from the environment.[16b, 56] These sites then enable the bonding process of different materials that would be otherwise incompatible with the surface. In this way, it is possible to bond polymers with polymers, various macromolecules, metals, etc. [57] An extremely large number of cases for improved bonding of polymer surfaces through precise functionalization have been reported in the scientific literature as well as in industrial practice.[16b, 56] Similarly for textiles, where grafting of functional groups and improved dye adhesion are the most common examples.[25, 58] This also holds for plasma prepared surfaces of other materials such as metals, ceramics, and cellulose. which can be functionalized in order to provide better bonding of polymers on their surface.[59] However, it is worth noticing that in some cases we are only dealing with plasma cleaning and removal of a very thin layer caused by ambient pollutants, such as organic vapours from surfaces.

In the future, this field is still expected to develop further and be the most common example of plasma application for any plastic or textile processing. This clean technology based on cold plasma is expected to grow at a lucrative Compound Annual Growth Rate (CAGR) of 16.2% from 2016 to 2021, to reach 2.48 billion EUR by 2021 from 1.17 billion EUR in 2016. [60] A large portion of this growth is expected to be facilitated in the field of plastics and textiles, due to the rising adoption of cold plasma in textile finishing and plastic surface processing as a cost-effective and ecologically benign technology replacement for predominantly wet chemical processing. This will be enabled by precise functionalization of surfaces with targeted functional groups, which might even enable switching of polymer and textile properties, such as superhydrophilicity and superhydrophobicity. A number of cases where plasma functionalization is playing the key role in improving surface properties is described in the following sections.

2.2 Precise functionalization for improved sensor performance

Conducting polymer materials have the ability to function as conductometric sensors for the detection of hazardous molecules (gases, biomolecules, volatile organic compounds, etc.) to ensure safety in various working environments.[61] In this section, the focus is directed towards the use of conducting polymers for the detection of various gas molecules or organic vapours. Conducting polymers are suitable for molecular detection at room temperature, which is a significant advantage over metal oxide based sensors.[62] Various wet chemical and ionized gas pre-treatments are utilized to balance the guest-host interactions which sequentially improve the selectivity and sensitivity of the fabricated sensors.[63]

It is known that plasma surface modification of conducting polymers such as polyaniline (PANI) has a prominent role in improving the sensing ability. A recent study showed that exposure of PANI to radio frequency O_2 plasma generated at 20 W and 30 Pa pressure for 1 min increased its sensitivity towards H_2 (about 30% increase in resistance towards 10 ppm H_2), whereas the same treatments decreased the sensitivity towards NH_3. The observed effects are explained on the basis of plasma induced chemical modification of the surface including carbon oxidation, removal of the protonated species and changes in the intrinsic oxidation state ([–N=]/[–NH–] ratio).[64] Nevertheless, the underlying mechanism remained elusive. In a recent study, researchers proposed a mechanism, taking amide like compounds as an example to probe the plasma functionalized PANI–analyte interactions.[65] It was proposed that plasma-incorporated functional groups can improve the sensitivity and response time by bringing the interacting molecule to its proximity through a completely reversible cyclic intermediate transition state (Figure 9). In the presented paper, the authors found that plasma functionalization decreased the response time to 16 ppm of urea from 9 s to 6 s with significant improvement in the sensitivity. On the basis of the proposed sensing mechanism, the sensitivity and selectivity can be tuned precisely by controlling the surface chemistry of polymer materials from the same class.

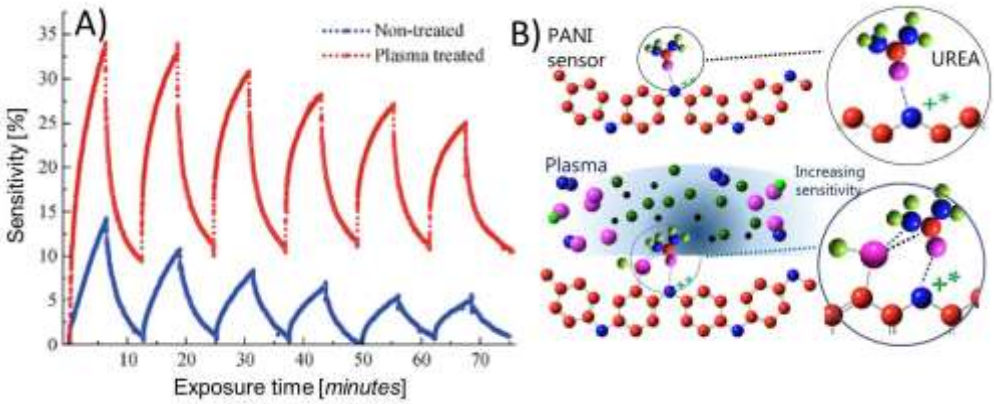

Figure 9. (a) Response of pristine and atmospheric pressure plasma treated PANI towards 15 ppm of urea and (b) sensing mechanism in pristine and plasma modified PANI. (Reproduced with permission from.[65] Courtesy and copyright: Higher Education Press and Springer-Verlag Berlin Heidelberg 2016.

Carbon nanotubes (CNTs) or graphene are two major classes of materials used for room temperature sensor applications. However, carbon allotrope-enabled sensors have a few disadvantages such as interference from humidity and non-linear sensitivity.[66] In many cases, this can be avoided by functionalizing with suitable conducting polymers, for example polyaniline (PANI) or polypyrrole (PPy).[67] Carbon nanostructures can provide suitable sites for nanostructure–polymer bonding that promote the conduction between two phases. The improved sensitivity or selectivity of such composites are ascribed to simultaneous electrical resistance changes in both phases due to doping/dedoping in the PANI phase and to electron transfer induced hole depletion in the CNT phase.[68] This bonding can be improved by exposure to a suitable reactive gas so that the plasma induced functional groups increase the adhesion strength by covalent interactions.[69] During such functionalization processes, the plasma treatments should be optimized so that any unwanted structural defects or morphological damage is avoided. For the controlled functionalization of carbonaceous materials without any thermal damage, various non-thermal plasmas rich in neutral atoms are more appropriate.[57c, 70]

Post-plasma treatments of various conducting polymer composites are also found to increase the sensitivity, as demonstrated by many researchers.[68a, 71] For example, the response amplitudes for radiofrequency O_2 plasma treated PANI-CNT composites were 2.3 (arbitrary units) towards 10 ppm of

NH_3 and pristine composite did not show any significant response. In this context, the improved sensing properties were explained on the basis of increased conduction channels after plasma surface etching.[71] Nevertheless, sensors fabricated solely from conducting polymers are preferred due to their low production costs and easy synthetic preparation routes. The sensitivity and selectivity can be varied based on multiple factors such as type of protonating agent, surface porosity, surface area and the extent of diffusion of the interacting molecule into the bulk of the sensor layer.[72] Many of these can be achieved by using plasma polymerization under optimized conditions.[73] Furthermore, *in-situ* doping of conducting polymers with suitable metallic particles allows proper tuning of the electrical properties of such materials, which is a crucial factor in sensing devices.[74] Such metal functionalization can be used for optimal sensor design aided by plasma polymerization or plasma enhanced chemical vapour deposition (PECVD) processes.[9][75] However, it should be noted that the use of metal composites derived from precious metals such as Pd, Au or Pt cannot be cost effective.

Despite its numerous advantages, plasma functionalization of macromolecules in sensor technology has some challenges to overcome in the near future. The major one is to avoid adverse effects such as aging of the plasma-incorporated functional groups that impedes the long term reproducibility of plasma functionalized sensors. Indeed, it is necessary to carry out more detailed theoretical investigations on the effects of various functional groups and their role in deciding the sensitivity and selectivity at a molecular level. This might light a way for the successful detection of single molecules in near future.

2.3 Environmentally-responsive polymers

The development of textiles that can respond to environmental signals and change their colour, swelling, conductivity and shape is becoming increasingly important for a wide range of applications, such as textiles for medicine, sports, aeronautics and military, sensing and protective textiles, drug delivery, diagnostics and tissue engineering textiles. Such textiles can be produced through the incorporation of stimuli-responsive materials, that respond to changes in temperature, pH, pressure, light and moisture by changing their structure (i.e. dyes which, under stimulus, become coloured or colourless), their physical state (i.e. from solid to liquid), or by changing their volume phase-transition (i.e. swelling and shrinking). [76]

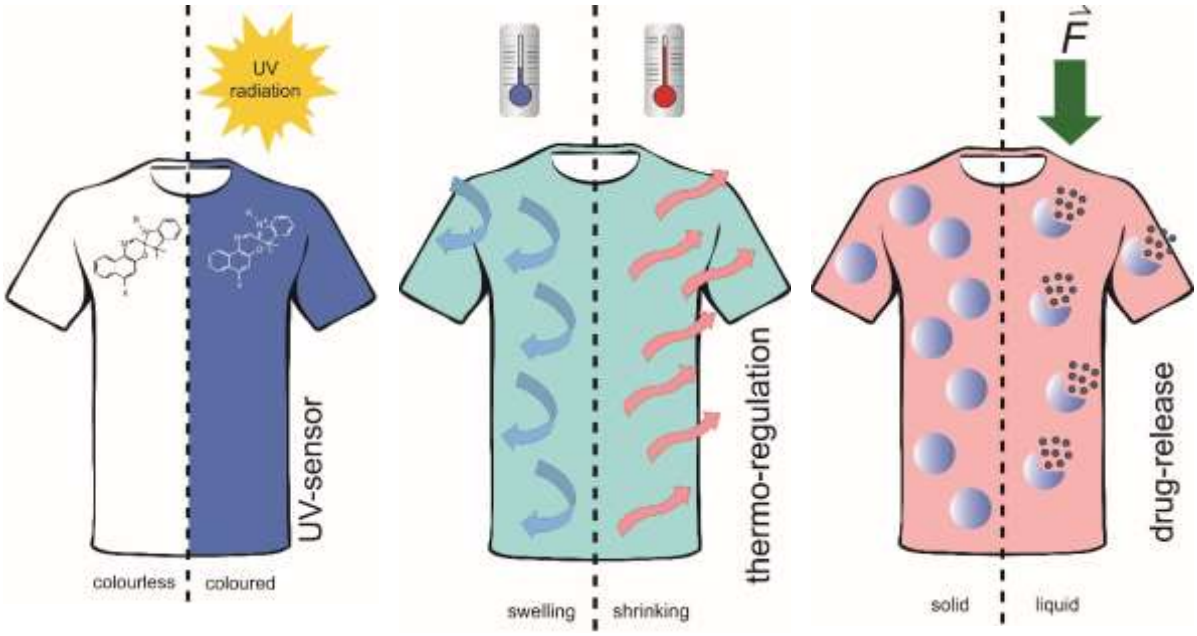

Figure 10. Presentation of some environmentally-responsive textiles and their mechanisms

Despite the great interest in the use of environmentally-responsive materials for textile applications, the technology has not yet been fully utilized due to the weak interaction, adsorption and adhesion between the responsive materials and textiles. The same chemical charge of the textile and responsive material (i.e. anionic cotton textile and anionic photochromic dye) or absence of the free polar functional groups on the textile (i.e. polyethylene) are the main reasons for poor bonding with other materials. [77]

In respect to that, the surface modification of textile materials by low-temperature plasma treatment has opened up new possibilities for their functional performance. [78] Depending on the final process requirements, the textiles treated with low-temperature plasma have increased surface roughness and changed reactivity due to incorporation of different functional groups (i.e. oxygen, nitrogen, fluoro). The increased surface roughness, induced by plasma, can enable the physical embedment of environmentally-responsive materials, while the changed reactivity of plasma-treated textile can enable their chemical adsorption.

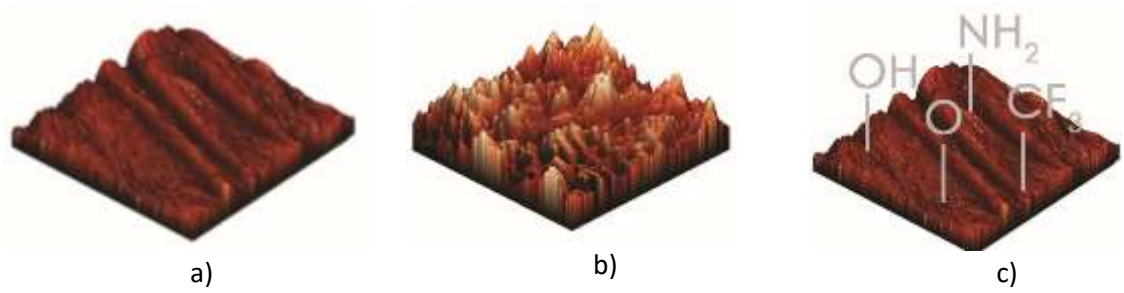

Figure 11. Atomic microscope images presenting the effects induced by plasma treatment on textile fibres: a) untreated textile fibre, b) changed surface roughness of fibre, and c) changed reactivity of fibre.

Only a few studies have been performed to increase the adsorption and adhesion of responsive materials onto textiles. This research was mostly focused on using atmospheric plasma systems, which gave promising results. [78b, 79] Treatment with air corona plasma increased the quantity of fragrance microcapsules on bamboo (cellulosic) fabric by 50%, when the textile was treated at the highest power. [79a] It was found that the power of air plasma treatment was in direct correlation with the number of microcapsules bonded to the fibres, due to the higher incorporation of carboxyl, hydroxyl and aldehyde groups. In the case where dielectric barrier discharge plasma (DBD) was used for modification of wool textile, the adsorption of phase-change microcapsules was much higher than on untreated wool. [78b] The reason was in the increased hydrophilic properties of wool. The water contact angle of wool decreased with increasing dosage (W min/m^2) DBD treatment, up to 88% (1250 W min/m^2). The incorporation of pH/temperature responsive microgel onto DBD plasma treated cotton resulted in covalent bonding between the microgel and cotton, and better adhesion. [79b] It was confirmed that microgel particles covered around 50% of cotton fibre surface. The best results of incorporation of microgel were obtained after nitrogen and argon plasma treatment.

The industrial scale production of "smart" textiles treated with plasma and environmentally-responsive materials is a considerable challenge for the future (Table 1). Over the next 10 years, it is very important to expand the lab-scale research through the use of different plasma systems (i.e. low-pressure, MW/RF discharge) and plasma working parameters (gases, pressure, power, etc.) in order to increase the adsorption and adhesion of a large selection of environmentally-responsive materials and textile materials. Another important future research area is the application of responsive materials on textiles *in situ* by using plasma polymerisation and deposition methods. [80]

Table 1. Problems, benefits and challenges of environmentally-responsive polymers.

Current problems in development of environmentally-responsive textiles: - *Weak interaction between textile and stimuli-responsive materials* - *Poor adsorption and adhesion of stimuli-responsive materials to 3D textile materials*
Benefits of using plasma for development of environmentally-responsive textiles: - *Increases adsorption of responsive materials onto textiles (up to 50%)* - *Increases the performance of textiles (up to 88%)*
Future research to be performed: - *Widen the lab-scale research on using plasma modification* - *Increase wash durability* - *Plasma deposition method of responsive materials on textiles*

2.4 Plasma micro-nano patterning

Plasma nanopatterning implies the use of a plasma to produce nanostructures on a surface. It represents a very promising technique since it constitutes a rapid, relatively simple and cost-effective process, and it can be realized on very large areas (cm^2) compared to other lithographic techniques.

Today, different approaches exist such as plasma assisted colloidal lithography (P-CL), plasma etching (PE), plasma lithography (PL), plasma assisted molecular beam epitaxy, plasma assisted atomic layer deposition (PE-ALD), etc., or a combination of these techniques. In the case of P-CL, the template can be modified by a prior reactive ion etching (RIE) step: the colloidal crystal (CC) is shrunk down by

thinning the particles and changing the inter-particle distance.[81] RIE has been used for many years before plasma started to be considered as a major technique for surface nanostructuring. P-CL implies the use of a sacrificial template constituted of a CC monolayer of silica (SIO_2) or polymer particles arranged in hexagonal compact structure deposited on the surface to be nanostructured.[82] The mask pattern is transferred onto the substrate through the interstices between the particles. In a last step the mask is removed either by PE or by wet etching. The positive or the negative of the mask pattern can be transferred to the underlying substrate in a top-down or bottom-up approach, respectively. A positive pattern is obtained when the material is deposited between the substrate and the mask and a PE is applied to remove the material between the particles. The uncovered regions are etched down whereas the regions protected by the colloids remain unchanged. A negative pattern results from the growth of another type of material between the particles of the mask using Plasma Enhanced Chemical Vapour Deposition (PECVD).[83] In a non-shadow deposition method, the material to be nanostructured is the mask itself.[84] In the PL method, polymeric materials are exposed to plasma for selective modification of the surface properties of the exposed areas.[85] Defects in the CC due to irregular arrangement of nanoparticles severely affects the uniformity of the nanopatterning. These defects turn to be an advantage in optics where irregularity improves the antireflective (AR) properties.[86] In biology, the uniformity is necessary for cell location. ''Mesh-assisted'' CL improves the uniformity and quality of CC over large areas.[87] Employment of binary CC masks enables the fabrication of improved masks, particularly when large particles can assist the self-assembly of smaller particles in-between the large ones.[83b]

Plasma nanopatterning is a rapidly evolving field, different techniques and applications are being explored. Recently, the range of nanostructured materials has broadened and this trend will accentuate in the next years. A comprehensive review of other options and nanoscale plasma-surface interactions can be found in the literature. [88] Several publications report on nanostructuring GaN surfaces.[89] Highly oriented pyrolytic graphite and glassy carbon surfaces could be patterned with nanopillars by P-CL and RIE.[90] Arrays of hexagonally arranged magnetic nanoparticles with narrow size distributions were fabricated starting from a polymeric matrix containing Pt and Fe particles.[91] The range of substrates being used for Plasma nanopatterning is also widening. Flexible and polymeric materials are now included in this technique (Figure 12a).[92] High-aspect-ratio structures of polymeric materials with a narrow gap were fabricated from bulk polymer materials using RIE.[93] Broadband AR and light-absorbing Teflon nanocone arrays coated with gold could be produced by PE of polystyrene bead monolayers on Teflon surfaces.[94] The variety of structures is also diversifying: pillars, frustums, cones, and nanofibers can be obtained simply by changing the etching duration, sphere diameter, or sphere material.[93] Asymmetric structures with high uniformity were fabricated through ICP-RIE treatment.[95] Metallic nanorings were produced by P-CL over large areas (0.7 cm^2).[96] Surface properties can be modulated by the height of the pillars and surface treatment. Amphiphobic and amphiphilic surfaces with ordered hierarchical topography were obtained by using a combination of P-CL and PL.[97] With a two-step etching process superoleophobic pillar arrays were produced. 3D nanopatterning is the most promising development for Plasma nanopatterning. Through a sequential passivation reactive ion etching (SPRIE) 2D CC arrangements were transcribed into well-ordered 3D architectures.[98] The deep reactive ion etching (DRIE) process is convenient to prepare ultra-high aspect ratio (ASR) Si nanowires (SiNWs).[99] Wire radii from below 100 nm to several micrometers, and ASR above 100:1 were fabricated by this method. The inverse structure of deep narrow holes (10μm deep and 500nm wide) was carved down playing on plasma chemistries (Figure 12b).[100] SPRIE is thus becoming a requisite method to produce high quality photonic crystals by adding a third dimension to 2D CC assemblies. Considering the trend for scaling down in Plasma nanopatterning, direct fabrication of silicon-based 3D photonic crystals will soon show photonic band gap in the visible region.

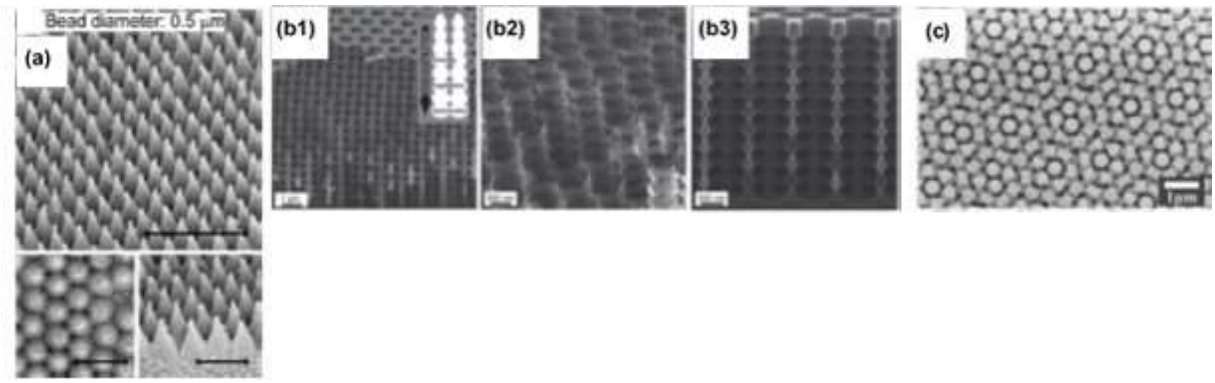

Figure 12. (a) SEM images of Teflon nanocone arrays fabricated with 0.5 μm PS beads. The top row shows large tilted views. In the bottom row, left and right images show top view and side view of nanocones, respectively. The scale bars indicate 2 and 1 μm, respectively. Reprinted with permission of ACS.[94] (b) SPRIE designs. b1,b2) Hexagonal, b3) lattices obtained using different colloidal nanosphere arrangements. Reprinted with permission of Wiley.[100] (c) Nanopattern of a bilayer crystal after RIE. Reprinted with permission of ACS.[101]

Direct applications of pattering can be found in optics, plasmonics and metamaterials to biosensing applications. Plasma nanopatterning directly affects the optical properties of the sample.[102] It is possible to produce wide-angle and broadband AR coatings: reflectivity of less than 1% over a wide spectral range (450− 900 nm) and a wide range of incident angles (0°−70°) can be measured on flexible nanocone-structured gold thin films.[94] This unique optical response is attributed to a combination of diffractive scattering loss from the periodic structure and localized plasmonic absorption from the rough gold film. In the years to come, broadband AR coatings are expected to be extended to other type of materials.

In plasmonics, 2D metallic gratings fabricated by P-CL exhibit interesting surface plasmon resonance (SPR) properties.[103] Enhancing the efficiency of photovoltaics is a main concern nowadays. These gratings will find applications where large-area light-trapping structures are needed.[104] Soon it will be possible to trap light in different wavelength ranges by changing the size of the PS beads that define the period of the grating. Plasmonics made by plasma nanopatterning open the door to the production of metamaterials.[96] Moiré CL provides an efficient technique for the fabrication of complex patterns on substrates by sequential azimuthal rotation of the CC mask (Figure 12c).[92, 101] By definition, metamaterials require small feature sizes and complex structures with multiple materials obliging plasma nanopatterning to reduce the usual pattern size of the colloidal mask.[105]

Plasma pattering can also be found as a new strategy for applications in biosensing. Ordered arrays of nanopillars improve the bioactivity of deposited proteins with respect to uniform films, leading to an enhancement in biorecognition. This novel templating technology is scalable and large-scale production of sensitive SPR substrates can be done for rapid and label-free detection of various chemical and biological analytes.[106] The sensitivity of the biorecognition device can increase.[107] Refractive index changes of the order of 10^{-5} can be detected. In bio recognition experiments, the good sensing performance of SiO_2-coated Si nanopillar array structures (limit of detection value of 5.2 ng/ml for bovine serum albumin (BSA)/antiBSA model) will be improved by increasing homogeneity and uniformity of the nanopillar array.[81b] Bio-adhesive properties of polymeric nanoholes surrounded by an antifouling matrix were shown.[108] Spatially controlled chemically heterogeneous surfaces able to

drive cell-alignment along a predefined direction can be prepared using polymer surfaces exhibiting tuneable properties at the nanometric scale.[83a, 109]

2.5 Combination of plasma with other technologies

In the manufacturing field, electrospinning and 3D printing represent cutting-edge technologies for the realization of added-value materials. In particular, electrospinning allows the production of nanofibers arranged to form highly porous meshes having a large surface-to-volume ratio, while 3D-printing allows the rapid prototyping of 3D models with complex geometries. Both technologies still present limitations related to production processes, e.g. the presence of defects in fibers of electrospun mats and layer delamination of 3D printed models; furthermore, additional processes may be required to modify surface properties of the products and allow their use for specific applications. To overcome these limits, atmospheric pressure plasma treatment can be combined with both electrospinning and 3D printing, both during the production phase and after the process for the treatment of the produced materials.

The electrospinning process allows the production of polymer, composite and ceramic nanofibrous mats with fibers whose diameter is in the range of submicron to nanometer. Electrospun mats are used as added value materials in different fields of application [110] in optoelectronics,[111] filtration,[112] catalysis,[113] energy scavenging,[114] nanocomposites,[115] as well as in the biomedical field,[116] for drug delivery,[117] wound dressing[118] and bone tissue engineering.[119] Focusing on polymer fibers, a high-voltage electric field is applied between a nozzle, through which a polymeric solution with its specific solvent is injected, and a collector (plane or drum) where the mat is deposited. Free charges are induced in the polymeric solution and move along the electric field with a low mobility in the fluid, thus transferring a tensile force to the polymeric solution; when the voltage reaches a critical value (in the order of a few kV), a fluid jet starts from the liquid droplet at the tip of the high voltage nozzle, thus leading to the formation of a Taylor cone. Because of the electrostatic repulsion between charges, the whipping instability occurs in the jet between the HV needle and the collector, inducing solvent evaporation and the formation of a dry fiber which deposits on the collector in a random or in an aligned way, forming a nanofibrous electrospun mat.[120] Among the most important variables in the process, the composition and concentration of the polymeric solution are crucial: indeed, a minimum concentration of polymer is required in order to allow the electrospinning of nanofibers. In addition, surface tension and viscoelastic properties of the polymer solution play a key role in the control of the quality of the fibers: beads being undesired defects in the fibers that reduce the mechanical properties of the electrospun mat and are possibly correlated to electrospinning of a solution with high surface tension or low viscosity;[121] therefore, a conventional strategy to improve the electrospinnability of a polymeric solution is the addition of a salt or of a highly polar solvent (usually with low vapor tension). Besides additional costs, safety and environmental concerns, electrospun mats contaminated by residues of incomplete evaporation of the solvent cannot be used for biological applications.[110] Thus, innovative tools for the control or even the elimination of beads formation avoiding the use of additives are required to overcome the current limitation of the electrospinning technology.

Cold atmospheric pressure plasma (CAP) can be used in combination with the electrospinning process: pre-treatment of polymeric solutions has recently emerged as a suitable tool to avoid beads formation in electrospun nanofibers. Indeed different studies demonstrated the possibility to improve electrospinnability of poly(ethylene oxide),[122] poly(l-lactic acid) [123] and poly(vinylidene fluoride), [124] PEO, PLLA and PVDF, respectively.

CAP treatment of PEO dissolved in water led to an increase of solution conductivity, viscosity, and surface tension and resulted in the production of beads-free nanofibers. Moreover, the crystalline phase of the polymer increased in electrospun fibers when using plasma pre-treated PEO solution: the authors suggest that plasma treatment ionizes the polymer chains in the fluids and thus they can be aligned in the electric field during the electrospinning process.[122]

The pre-treatment of a small volume (12 ml) of PLLA in a 100% dichloromethane solution enabled bead-free mats used for biomedical applications to be obtained, avoiding the conventional use of an additional high-boiling point solvent (dimethylformamide), as can be seen in Figure 13.[123] Reactive species together with charged molecules produced during the CAP treatment, play a crucial role in the improvement of electrospinnability induced in the polymeric solution. Finally, an increase of the solution viscosity and a "light" crosslinking (or increase of the average molecular weight) of the chains can be achieved performing a pretreatment of PVDF electrospinning solution, thus enabling the production of defect-free nanofibers, with an improvement of both mechanical properties and electrolyte uptake.[124]

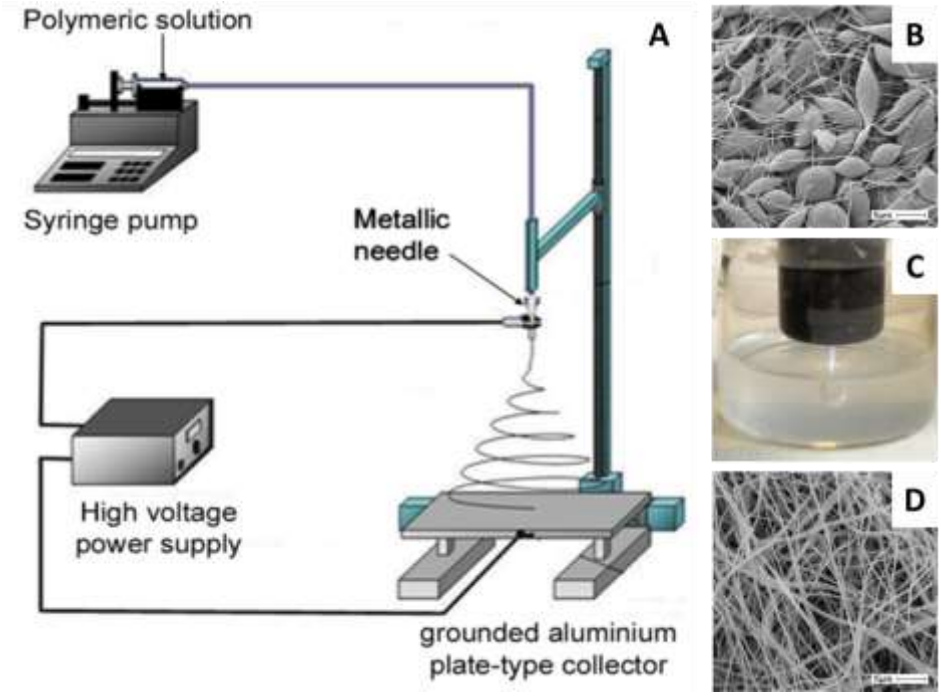

Figure 13. A: Schematic of an electrospinning apparatus, B: SEM images of fibers obtained from PLLA polymeric solution, C: pretreatment of polymeric solution by means of nanosecond pulsed plasma jet, D: SEM images of fibers obtained from plasma treated solution.[123a]

In summary, even though further investigations are required to elucidate the mechanisms behind the improvement of spinnability of pre-treated solutions; the CAP treatment can be synergistically implemented during the electrospinning processes to overcome limitations of the technology. Further efforts must be directed toward the scaling up of the process in terms of CAP efficacy in the improvement of the electrospinnability of hundreds of millilitres of polymeric solution. It is well established that CAP treatments can modify surface properties, improve wettability, and induce crosslinking of polymer films and these effect can be induced also in electrospun mats.[125]

3D printing is an additive manufacturing process producing 3D objects with geometric complex shapes in different materials (plastics, resins, ceramics, composites and metals) and based on a layer-by- layer

approach starting directly from CAD data.[126] 3D printed products can be used in several different fields: microfluidics,[127] electronics,[128] medical training,[129] biomedical engineering,[129] tissue scaffolding,[129-130] high-performance structural materials,[131] and production of mass-customized products.[132] Fused deposition modeling (FDM) fabricates 3D polymeric models extruding thermoplastic filaments from a moving extruder through a heated nozzle and depositing the semi-molten materials layer by layer: the nozzle movement traces the design of horizontal cross-sections of the model and at the same time extrudes the polymers that solidifies in the desired areas (Figure 14).[128] Current limitations of this technology are mostly related to the weak bonding between layers, leading to delamination and causing the failure of the product,[132] and, in the biomedical field, the low biocompability of the materials used for the production of 3D printed scaffolds.[130a, 133]

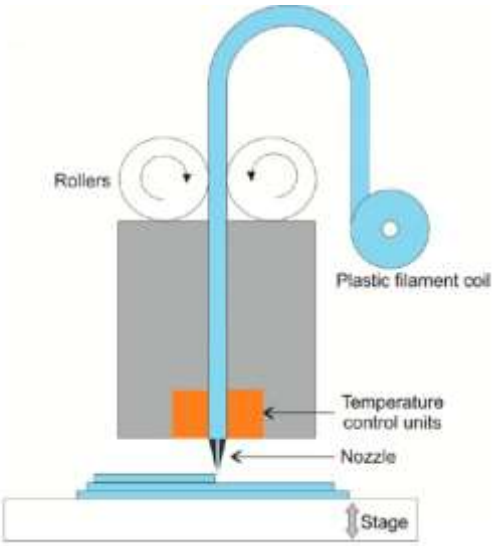

Figure 14. Schematic of an FDM 3D printer.[128]

For plasma in combination with 3D printing, the state-of-the-art reports mainly on the patent side, on the possibility to implement CAP treatments during 3D printing processes with the main aim of improving layer adhesion of the models: indeed, some patents deal with CAP sources coupled with extruders to treat the polymer during the deposition to improve bonding and surface adhesion between layers,[134] but a deeper investigation on the possible positive implications stemming from the combination of these two technologies is still required: quantitative data on the modification of layer bond strength and reduction of product delamination are missing. On the other side, it is well known that plasma post treatment of 3D printed products can modify their surface properties: both plasma polymerization and atmospheric [135] or low pressure oxygen plasma treatment [136] of 3D printed scaffolds induce an increase of both hydrophilicity and nano-scale roughness, leading to an increase of biocompatibility. Furthermore, the low pressure plasma treatment induces an improvement of the adhesion strength between a textile polymeric fabric and the objects 3D printed on it, caused by an increase in hydrophilicity and wettability of the fabric surface:[137] accordingly, post process treatments can be performed replacing extruders with a CAP source in the head of the pantograph of commercial 3D printers. [138]

2.6 Abrasion resistance

Abrasion resistance is a strongly desired material property in many applications. It is mainly dominated by the materials surface disregarding the material being a metal [139] or a polymer.[140] Plasma processes

have successfully been able to combine specific bulk material properties of the work-piece with a tailored surface property.[141] Typical plasma deposited materials benefiting wear resistance or improved implant lifetime have been diamond like carbon (DLC) films.[142] In the case of metals, plasma nitriding process steps are used to harden the upper layers of the component.[143] Glassy thin films (SiO_2 like films) with a high degree of cross-linkage are deposited using organosilicon compounds (gases and liquids) as precursors for the plasma enhanced chemical vapour depositions (PECVD).[25, 144] These coatings also act as an anti-scratch protection for soft surfaces. Using a combination of nanomaterials with polymer matrices is a more recent development that has led to more controlled plasma deposited thin film properties.[145] Plasma processing generates changes in surface properties through three main mechanisms that can all be used to improve abrasion resistance of the treated material. Change of morphology,[146] or change of porosity, both result in a change of friction properties that reduce wear as well as the application of a wear resistant hard coating.

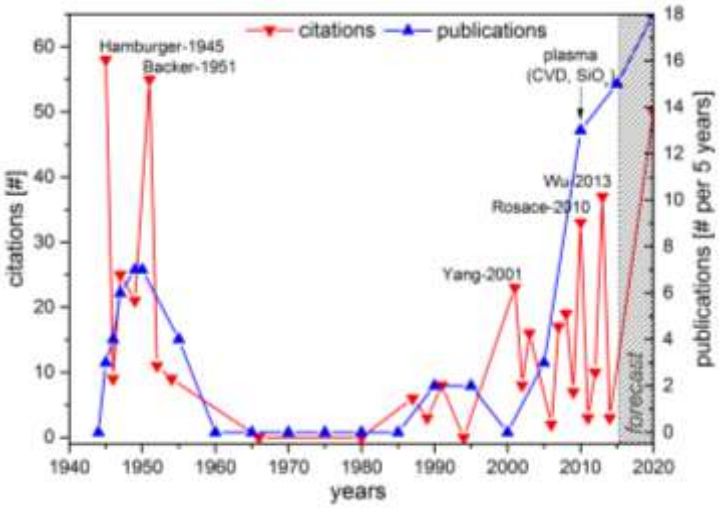

Figure 15. Publication indicators for studies on abrasion of textiles (data based on Web of Science, record date Jan. 2016).

A publication analysis of abrasion and textiles reveals the following insights. Figure 15 presents the publications (red) that rate the indicator of the scientific interests and citations of the corresponding publications in blue rate the scientific relevance of the topic. For the first time, the interest on the topic of textiles and abrasion resistance arises after 1945. The early works report on results obtained by wear testing, but they did not treat the causes of failure. Systematic investigation of material properties that are responsible for abrasion of textiles, has been published by Hamburger in 1945.[147] Here, different synthetic materials (acetate, viscose, nylon) are tested and the measurable changes by abrasion are explained purely by fundamental properties (modulus of elasticity, creep rates, etc.). In the study by Backer *et al.*, the important effect of structural geometry is considered.[148] For this publication, the scientific interest correlates with the relevance of the topic. The number of citations is maximal for studies in 1950 and has never been exceeded by any later studies. The relevance of the topic played an important role for military applications in the time of the cold war, when durable textiles were developed and tested (various cotton fabrics for army in [148]).

The second important surge of publication characteristics for the abrasion resistance of textiles begins after the year 2000. The rising interest in textile abrasion resistance can probably be attributed to the availability of new technology, as well as the growing commercial interest in abrasion resistance for the growing market of outdoor clothing and textile products. The investigations focus also on

mechanical improvement of textiles by post-treatment. The role of plasma for the textile treatment in the last period has been reported by Zille, Oliveira and Souto in 2015.[36] Yang and Qian report 2001 on the effects of high temperature exposure and on role of chemical effects (acid-catalyzed depolymerization, crosslinking by 1,2,3,4-butanetetracarboxylica acid).[149] In 2010, the silicon oxides ($SiO_xC_yH_z$) films were deposited by means of plasma enhanced CVD by Rosace *et al.*[150] Four textiles (cotton, cotton/silk, polyester, cotton/polyester) were coated, and a significant improvement of the abrasion resistance observed. The number of rubs at the end-point (35,000) of the test was doubled for the coated cotton/silk textiles compared to the untreated textile. Despite the treatment being based on low-pressure plasma technology, it is an obvious motivation for the deposition experiments developed at atmospheric pressure.[151] An optimized treatment of the textiles with SiO_x coating at atmospheric pressure can play a crucial role for the reduction of abrasion in future. As demonstrated in [152], an addition of just 3 % of SiO_2 nanoparticles in the starch used for textile fibers improve the wear resistance significantly. This represents a chance for atmospheric pressure deposition processes, because of their flexibility to coat surfaces either with uniform SiO_x films or with SiO_2–like particles.

The increasing interest in plasma processes for applications in textile production is due both to added value and the new pollution-free non-wet chemical technologies.[25, 153] 16a].[16a] This is especially targeted for roll-to-roll processes, where atmospheric pressure plasma processes are irreplaceable in textile processing. Here, the corona based and DBD based processes have dominated industrial processes. [17, 154] Plasma based processes improve textile properties such as felting properties for wool, which drastically changes the mechanical properties of wool fabric and makes it more rigid,[155] which is attributed to the morphological changes of the wool fibre. Fibres are also used in composites, where plasma processes can improve the binding strength between the fabric and resin.[156]

Generally, the trend in fabric and polymer surface functionalization goes towards influencing multiple properties such as abrasion resistance, optical properties such as anti-reflectance as well as wetting behaviour, as was the case for ophthalmologic lenses reported in [157]. Typical abrasion resistance coating materials such as SiO_x or DLC that have been used to improve wear resistance for biomedical applications,[142] change several properties of fabrics such as antibacterial properties of cotton,[158] biocompatibility for e.g. textile blood vessels [159] or wettability of textiles. Metallic coatings are often used to improve anti-static; electrical conductivity; electromagnetic shielding or heat protective properties.[160] However, these coatings are often of low adhesiveness to the textile substrate leading to a very low abrasion resistance of the technical fabric. Here, layered films will be able to generate a combined functionality. Novel materials can also improve abrasion resistance of fabric by introducing self-healing properties e.g. after ironing.[152]

Future challenges of coating fabrics with plasma-based materials for abrasion resistance will be in generating hard coatings that can withstand the mechanical strain that fabric movement causes. For this, composite coatings are ideally suited. Future technology will need to implement hierarchical structures by combining different process technologies. Combination of nano-, micro, and macro structures within the coating and of the fabric itself will improve lifetime and abrasion resistance by one to two orders of magnitude. However, not only the coating processes need to be developed, also tests of abrasion and wear resistance may have to be different than standard tests on hard substrates. Bdinsky *et al.* [161] found that the more easily the material deforms in contact with a particular abrasive, the better the abrasion resistance. Typical wear resistance tests such as pin-on-disc tests used for hard substrates need to be adapted to meet the requirements of textile coatings. Finally, the abrasion resistance of textiles has been approached by plasma based and non-plasma based processes including atmospheric pressure plasma based processes. However, the needed improvement of fabric abrasion resistance is still missing.

3. Design of complex surface coatings including those with macromolecules and nanomaterials

3.1 Antibacterial coatings

Nowadays, the engineering of new materials with antibacterial properties receives a lot of interest from the industrial, medical, and healthcare sectors. Market analysis shows a high level of industrial demand mostly from the textile and plastics industry. Recent transparency market research observed that the antimicrobial coatings demand was worth USD 1.6 billion in 2012 and is estimated to reach USD 3.3 billion by 2018, growing at a CAGR of over 12%.[162] The biomedical requirements of a material in terms of physical, chemical and mechanical properties results in a shift in a technology from embedding antibacterial agents in the matrix structure of composites to the engineering of surfaces possessing high antibacterial activity. The foremost strategy is considered to consist of deposition of a thin layer of antibacterial coating on the top surface of materials, such as non-woven fabrics (bandages, wound textile, medical masks) so that only the surface of the material will change and bulk properties are not affected. Such processes preserve all the properties of the bulk material as only a thin layer of 10 - 500 nm is deposited. A general trend in this research area is to develop coatings with advanced properties of low toxicity, high antibacterial efficiency, highly controllable release of the antibacterial agent even through external triggering the coatings performance. Some of the most promising strategies are presented in Figure 16.

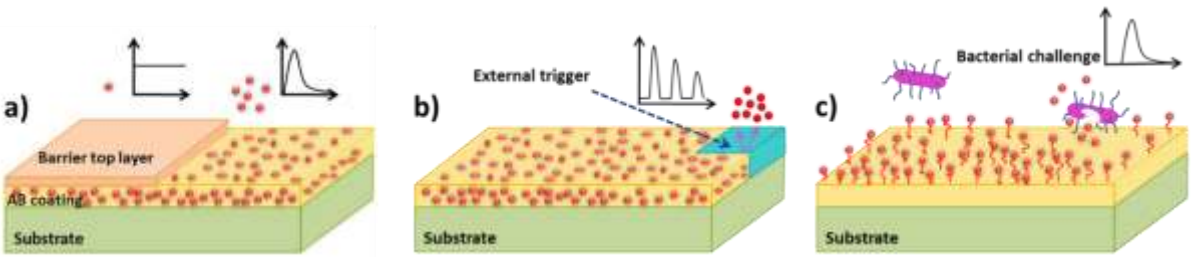

Figure 16. Advanced antibacterial coating strategies: a) use of the barrier layer for control of the drug release from long lasting release kinetics to peak release kinetics; b) external triggering the release by pH, temperature, magnetic or light field; c) use of green coatings with antibacterial agent targeting specific bacteria.

Among different surface engineering methods the current state-of-the art technologies are:

- surfaces with designed morphology and micropatterns,[163]
- surfaces with attached chemical groups,[164]
- surfaces with coatings incorporating antibiotic agents,[165]
- surfaces with green antibacterial coatings.[166]

One approach is to change the surface morphology in order to prevent microorganisms attaching to the substrate which provides a convenient way to avoid biofouling. However, the modified surface does not release antibacterial compounds and usually sole use of such materials as antibacterials is rather limited. Anchoring or grafting antibacterial agents on the topmost surface of substrates using wet chemistry has been considered to enhance the efficiency of incorporation. In general, chemical or plasma pre-treatment of substrates is implemented in order to introduce chemical groups such as

amine groups [167] or sulfonated groups.[168] Then, substrates are immersed into a solution of antibiotic or another antibacterial agent in order to load a drug (typically less than 2%).

In the case of biofilm formation, systemic use of antibiotics is not sufficient due to limited penetration of drugs into the biofilm. One of the strategies to overcome this problem is with synthesis of antibiotic releasing coatings. While such coatings are already in use in sutures and central venous and urinary tract catheters, the coatings for orthopaedic implants are still mainly at a research phase. The most frequently used antibiotics that have been incorporated into different coatings are gentamicin, vancomycin, rifampicin, tobramycin, carbenicilin and amoxicillin.[169] Due to increasing concerns about bacterial resistance to antibiotics and the increased number of antibiotic-resistant strains, the coating industry has a strong motivation to find alternative antimicrobial agents that are not relying on the classic antibiotic mechanisms. The strategy of using so called "green coatings" that contain natural antimicrobial agents, such as various biopolymers (chitosan, hyaluronic acid), bacteriocins, microbial peptides, probiotic bacteria, and various combinations of them is under intensive investigation. Because of their natural origin they have beneficial properties, they are not toxic, non-immunogenic, biocompatible and their production is inexpensive. Chitosan is probably the most studied material so far. The exact mechanisms of its antimicrobial action is not fully understood, but the most acceptable being the formation of electrostatic interactions between positively charged molecules of chitosan and negatively charged bacterial membranes resulting in inhibited cell growth due to changes in membrane permeability. The drawback of chitosan is its insolubility in water, high viscosity and tendency to coagulate with proteins thus limiting its use. The renewed interest in alternatives to antibiotic drug loaded coatings for medical devices has driven focus toward bacteriophage coatings. Phages, which have the natural ability to specifically target and eliminate their bacterial hosts without damage to mammalian cells, are an attractive alternative to synthetic antimicrobial agents, see Fig.15 c). However, the applications of phages for *in vivo* treatments have some drawbacks including specificity to bacterial species and development bacteria resistance to phage attack.[170] However, research and application of the coating based on bacteriophages are likely to be one of the priorities in the field of antibacterial materials engineering.

A promising approach for the deposition of antibacterial coatings on an industrial scale is plasma assisted polymerization. Thin films composed of silver nanoparticles in a polymer matrix can be deposited by combining plasma polymerization and silver sputtering at low pressure.[171] The content of silver ranges from a very small percentage to as large as 29%.[172] The expensive low pressure plasma deposition system has the limitation of low deposition rate that is motivating industry to move from sub-atmospheric to atmospheric pressure processing. As an alternative to antibiotic loaded coatings and green coatings, nowadays considerable attention is paid to antibacterial coatings with incorporated nano-particles of metals and metal oxides. Due to their large surface-to-volume ratios and small size, nanoparticles have emerged as a new generation of antibacterial agent.[173] Unfortunately, the emergence of cytotoxicity and genotoxicity of metal nanoparticles goes against practical applications in the human body.[174] Considering these concerns, research has been focused on antibacterial surfaces with firmly loaded nano-materials with a precise release of the antibacterial constituent from the material by deposition of a barrier layer. In this way, the release of nanoparticles to the microenvironment can be limited. Vasilev *et al.* developed a tuneable antimicrobial triple-layer coating based on amine polymer films loaded with silver nanoparticles.[175] With an appropriate thickness of the plasma polymer below 100 nm, the nanocomposite films were feasible to maintain efficient antimicrobial activity and to support the growth of mammalian cells. Deng *et al.* developed PET non-woven fabrics with antimicrobial properties by firmly immobilizing silver nanoparticles via a double layer of plasma deposited organic films.[176] The obtained coatings had high durability of silver nanoparticles bonding in the matrix and high antimicrobial efficiency against *P. aeruginosa*, *S. aureus* and *C. albicans*.

While antimicrobial surfaces have been sought since the early Phoenicians, the persistent research is illustrative of the complexity of the topic. The sheer number of technological boundaries that still remain include substrate specificity, durability, ease of application, efficiency, broad spectrum of activity and environmental safety. Although a large number of demonstrated effective treatments are available, current methods suffer from complex and multistep processes, the use of toxic antimicrobial agents, excessive leaching or slow but finite release, or rigid matrixes. Using plasma technology, energy and chemical resources can be limited while very thin layers about 100 nm of well bound coatings can be deposited. The effectiveness of plasma treatment for developing antimicrobial coatings has been proven and the challenge now is to extend this technology towards industry. However, obstacles such as coating biocompatibility, controllable release of antibacterial agents, ease of implantation in materials production line and processing speed need to be tackled in order to pave the way for a new generation of antibacterial products.

3.2 Biomimetic coatings

Biomimetics is a relatively new interdisciplinary research field that is defined a study of the formation, structure, or functions of biologically produced substances and materials and biological mechanisms and processes with the main intention of synthesizing similar products by artificial mechanisms which mimic natural ones.[177] Although, the fascination in diversity of nature's "inventions" is as old as civilization, the field of biomimetics has experienced massive development from 1990's. This can be evidenced by the number of articles published in high level scientific journals: for instance, in the year 2016 alone, according to the web of science database over 1000 scientific articles were published containing the words "*bioinspired*" or "*biomimetic*" in their titles. Such increased interest in bioinspired materials or smart solutions has been enabled by the confluence of rapid progress in biology, chemistry and physics that enabled a deeper understanding of the principles of function of biological systems and advances in nanotechology that made it possible to design and manipulate materials on a submicron scale.

An iconic example of bio-inspiration is the lotus leaf. Due to their multiscale surface roughness and chemical structure lotus leaves are super-hydrophobic, low adhesion and dirt-resistant.[177] However, many other examples of multifunctionality of biological materials may be found such as super-hydrophobicity and anti-reflection of cicada wings, drag reduction and anti-biofouling of shark skin, anisotropic wettability of rice leaves, super-hydrophobicity, structural colour and high adhesion of rose petals. In addition, nature has developed smart solutions that enable a response to external stimuli with no or only minimal energy consumption. Typical examples of this are the chromatic mimetism of camaleonts or hygroscopic movement of pine cones. Many of these concepts are nowadays models for fabrication of advanced products such as water-oil separation membranes, anti-dust, anti-fogging, anti-icing or anti-reflection materials, textiles with color changes on demand, smart textiles with automatic thermal or wettability regulation or UV-radiation protection, drug delivery systems, self-healing fibers or packages.[177-178]

The common characteristics of the above given examples are a combination of surface chemical composition, multiscale surface topography from nano- to micro-scale and/or stimuli-responsive character of materials. All of these material properties were already addressed by the plasma community in numerous studies with some very impressive results.

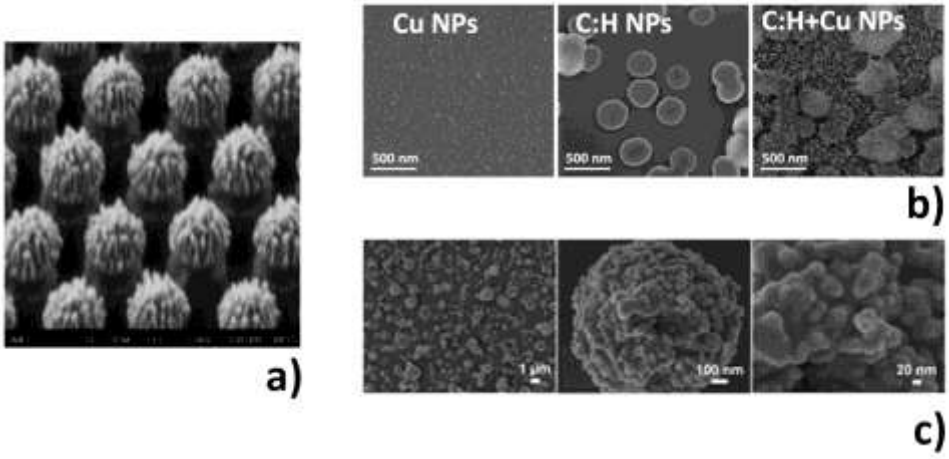

Figure 17. a) SEM image of hierarchical (triple-scale) roughness micropillars produced by the combination of colloidal lithography of 1 µm particles followed by plasma etching. Reprinted with permission from Ellinas *et al.*[97] b) SEM images of Cu NPs, C:H NPs and C:H NPs decorated by Cu NPs and overcoated with plasma polymerized n-hexane. Reprinted with permission from Petr *et al.* [179] c) SEM images of NC coating deposited for 10 min in a DBD fed with He and the aerosol of a 3 wt % oleate-capped ZnO NPs dispersion in n-octane. Reprinted with permission from Fanelli *et al.* [180]

For instance, nanostructured, multiscale, hierarchical structures responsible for super-hydrophobicity were produced by a lithographic step followed by etching and then nanotexturing steps. Examples of this are published by the Demokritos group (Figure 17a).[97] Alternatively, surfaces with multiscale roughness were obtained by assembly of nanoparticles with different sizes produced by means of gas aggregation sources based on plasma technologies and coated with thin film of plasma deposited polymers (Figure 17b),[179, 181] or by aerosol assisted plasma deposition (Figure 17c).[180]

Stimuli responsive materials were either grafted onto plasma activated substrates,[182] or deposited in the form of thin films by a PE-CVD processes.[80b, 183] One possibility to achieve this is the grafting of polymer brushes onto plasma modified surfaces. These polymer brushes are stimuli-responsive concerning pH-value or temperature, resulting in a changed surface wettability or cell proliferation, for example.

In spite of these successes the wider spread of plasma based technologies for the production of biomimetic materials is still rather limited. To increase their penetration the following tasks should be addressed in the next 10 years:

a) *Scale-up of processes and cost reduction*. This is general problem of many other plasma-based technologies that has to be addressed in close co-operation with industry. Moreover, this task implies the development of new plasma sources and diagnostics methods to be applied in-line for process control.
b) *Widen the range of nanomaterials with proper functionalities*. Numerous techniques were developed and tested within the past decades that enabled the production of various kinds of nanomaterials ranging from nanoparticles, nanowires, nanocolumnar structures or nanocomposites. Further developments in the biomimetic field may be triggered by controlled and tailorable fabrication of multi-component nanoparticles through plasma based techniques. First attempts made using gas aggregation sources are promising.[184] Additionally, new strategies to test the performance of the produced nanomaterials should be considered, such as the use of one or multi-dimensional gradients of studied parameters that could lead to a fast identification of optimal structures. In addition, industry standardized tests and testing methods (e.g. DIN) have to be considered and used to fulfil the demand of quality testing under industrial conditions and to increase the chance of transferring these results into large series production.
c) *Widen the range and performance of materials capable to respond to external stimuli*. New approaches must be developed that will assure the persistence of the chemical structure needed for response to external stimuli such as temperature, light, electrical field, humidity and pH. Promising strategies that are currently the centre of attention are plasma assisted vacuum thermal decomposition that provide exceptional control over the level of cross-linking of plasma deposited polymers,[185] or nanomaterials synthesis using plasma generation in liquids.[186] In terms of plasma assisted polymerization in the liquid phase, this was reported to enable the retention of the monomer chemical composition,[187] or to the formation of covalent bonds between the activated substrate and growing film.[188] However, new diagnostics methods as well as the development of models that shed light on to the complex phenomena of plasma-liquid-biomolecule interaction is needed to enable further developments in this direction.
d) *Integration of multiple functions*. Although plasma based techniques were demonstrated in the past to be capable of modifying textiles or plastics to provide a particular functionality the vision for the next decade is to combine more functionalities in a single material. This challenge is reachable by a combination of different deposition/modification approaches.

e) *Composites with embedded liquids, biomolecules or even biological systems*. Incorporation of liquids, biomolecules or even more complex biological systems such as cells in combination with a proper selection of matrix materials opens new research and application areas for production of advanced drug delivery systems, new generation of implants or for self-healing materials. The first experiments in this area were already performed using aerosol-assisted atmospheric cold plasma deposition.[189]

f) *Combination of different technologies.* To achieve all of the above mentioned goals the combined use off different technologies will be unavoidable. This includes wet-chemical processes (e.g. galvanization, dipping and varnishing), plasma technology, laser technology as well as pure mechanical methods (e.g. corundum blasting, polishing and emery), plus many more.

3.3 Drug delivery coatings

Textile materials have unique properties that allow for their use in multiple applications, from conventional to high-tech. In this context, medical textiles (textiles for use in any of a variety of medical applications, including implantable applications) can play a significant role in benefiting our ageing society that may need novel solutions that differ from conventional approaches.

Drug delivery is a term that refers to the administration of a pharmaceutical compound to humans or animals. Most common methods of delivery include the preferred non-invasive oral, nasal, rectal, topical dermal and transdermal routes. Current investigations in the area of drug delivery systems include the development of targeted delivery in which the drug is only active in the target area of the body and drug formulations which are released over a predetermined period of time in a sustained and controlled manner from a formulation: controlled drug delivery. When these concepts are applied to textiles, innovative medical textiles can be designed, conferring an important added value to the primary function of such materials, and in this sense, plasmas can provide an alternative approach in the design of medical textiles with drug delivery capabilities.

Moreover, in contrast with polymer films, the particular features of textiles (Figure 18) have to be carefully taken into account when thinking of applying plasma treatments onto them or withstanding the application of molecules such as drugs and active principles for pharmaceutical or cosmetic applications. Textile fibres are characterized by a high length vs. diameter, high tenacity and elasticity. Plasma treatments on laminar textile structures show important differences compared to polymeric films, since the three-dimensionality of the material, and the differences in construction of the yarns, result in more complex diffusion phenomena, so the uniformity of the plasma effects must be taken into account when designing materials and treatments for specific applications.

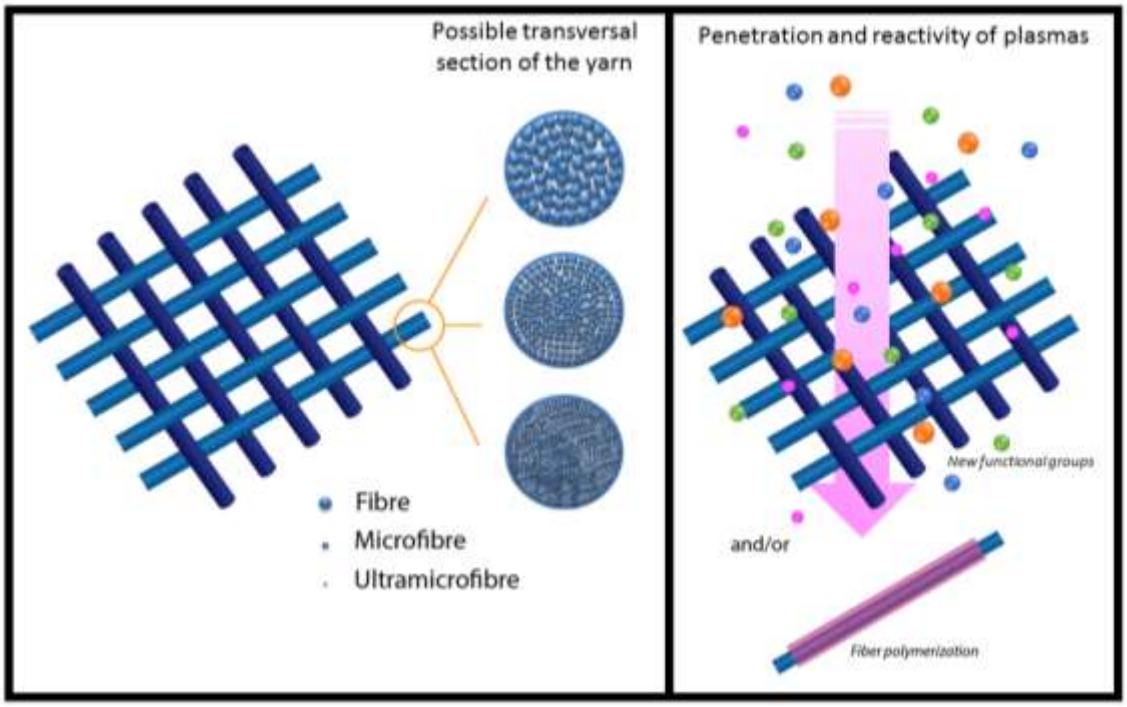

Figure 18. Reactivity and penetration of plasmas through textiles depend on the construction of the textile (woven, knitted, nonwoven) and on the fibre dimensions which constitute the yarn/multifilament and may lead to significantly different specific surface area (i.e. for a 20 tex yarn, the number of fibres in its transversal section might vary from 153 fibres, to 500 microfibres or 2000 ultramicrofibres, leading, respectively, to a specific surface area of 32 cm^2, 60 cm^2 or 113 cm^2 (for a 1 cm^2 of a fabric with 30×30 yarns)).

Textile-based drug delivery systems can be divided into two main categories: non-implantable textile materials for topical and transdermal applications, and implantable medical textiles.

Plasma treatment of non-implantable textiles aimed for topical and transdermal applications. Traditional wound dressings include mainly natural (i.e. cotton and cellulose) or synthetic (e.g. polyamide (PA), polypropylene (PP), etc.) bandages and gauzes which perform different functions. Unlike topical pharmaceutical formulations (gels and ointments), these dressings are dry and do not provide a moist wound environment. They may be used as primary or secondary dressings, or be part of a composite of several dressings, each performing a specific function. These textiles can be employed either in topical or transdermal drug delivery. While topical drug delivery applications refer to the local treatment of a dermatological condition,[190] such as the treatment of dermatological conditions such as eczema or psoriasis, transdermal drug delivery refers to the administration of active compounds in discrete dosage forms through the skin (at a controlled rate and concentration) to the systemic circulation. The transdermal route has numerous advantages over the more traditional drug delivery routes. These include high bioavailability, absence of first pass hepatic metabolism, steady drug plasma concentrations, and the fact that therapy is non-invasive; but, the drawback is having to cross the efficient barrier layer of the skin. Thus, the use of textile dressings, whose surface is directly in contact with the skin, is an ideal vector for such molecule delivery.

In general, if drugs are incorporated directly into textiles without any additional agent or mechanism, the release of the drug is very fast and not suitable for a controlled drug delivery. Therefore, different means have been studied to limit drug release within a certain timeframe and achieve the release of an active ingredient to its topical therapeutic concentration for a predetermined time period, such as coating of the fibers with different biocompatible polymers through wet processes, incorporating

microcapsules entrapping the drug, or even more complex approaches such as the use of hollow fibers as drug reservoirs[191] or electrospun nanofibers with a high surface area to volume ratio[192] which allow for simultaneous spinning of the fibre-forming solution together with the desired drug.[192-193] In a simpler and environmentally friendly approach, according to the kind of plasma treatment, diverse functional groups can be introduced on the target surface to improve biocompatibility or to allow subsequent covalent immobilization of various bioactive molecules. For example, plasma treatments with oxygen, ammonia, or air can generate carboxyl groups or amine groups on the surface, concomitantly with the elimination of surface contaminants.

The first works evaluating plasma with functionalizing gases on textiles for drug delivery utilized different drugs and plasma configurations. Labay *et al*.[194] employed atmospheric (corona) plasma treatments of PP and PA fabrics to study the release of a non-steroidal anti-inflammatory (NSAID) drug (ketoprofen) for topical treatment of rheumatoid arthritis. In another approach, low pressure air plasma was investigated to combine the advantages of PA compressive stockings (providing improved venous return) with an active principle (caffeine) with action on body lipids (cellulite) for cosmetic applications.[195] Depending on the lipophilicity of the drug, the improved wettability and surface functionalization of the fibers by plasma led to higher drug loadings in the fiber (40% more ampicillin on corona plasma treated PP).[57a] More recently, Choudhury *et al.* employed low pressure oxygen plasma with similar results, finding an increased 17% amoxicillin impregnation on silk fibroin sutures that displayed extended drug release over 14 days and were efficient in vivo. In all the previous cases burst release profiles were observed.[196] Ar:O_2 low pressure treatments were studied by Mogal *et al*. on polylactide-co-glycolide films, observing improved – though limited (6% more) drug release as in the aforementioned works on textiles.[194-195, 197] However, it has to be noted that plasma functionalization alone, though very efficient for increasing drug loading, is not sufficient to provide an accurate control over the release of the drugs from polymers of textiles (i.e. 10% higher percentage of ketoprofen released but without changes in the drug delivery profile or 70% higher caffeine released with slight changes in release kinetics). Plasma polymerization on textiles and polymer films has been evaluated, in view of implantable devices and is reported in the following section.

Plasma treatment of implantable medical textiles used as drug delivery systems. Implantable textiles are used in effecting repair to the body whether it is wound closure (sutures) or replacement surgery (i.e. Hernia repair) and are thus employed as implants. PA has been used mainly for artificial ligaments, tendons and artificial joints, and recently for artificial hip prostheses and inguinal meshes.[198] PP is the least reactive polymer together with polytetrafluoroethylene (PTFE) and polyester (PES) and one of the most employed in abdominal repair surgery. The wide variety of polymers employed in the construction of such implantable textiles (Table 2) has to be taken into account when designing plasma treatments to enhance the fibre-drug interaction in view of achieving a controlled drug delivery. Implantable medical textiles have the advantage of being placed in the site potentially benefiting from a drug therapy, so they can be used as local drug delivery systems combining their main functionality with a therapeutic added value. The main objective of these new active prostheses is not only to restore a damaged function, but to also prompt tissue integration,[199] avoid periprosthetic inflammation[200] and prevent surface contamination.[201] Therein, different drugs may be delivered depending on the pathology. For instance, antibiotic-loaded implants can be a solution to avoid device-associated infections that are the result of bacterial adhesion and subsequent bio-film formation at the implantation site.[202] Postoperative antibiotic-based infection prophylaxis is usually administered following mesh implantation. But, even after decades of routine use, its capacity to minimize mesh-related infection is still a matter of debate and prevention remains a priority.[203] Thus, some works have investigated wet processes to produce biodegradable coatings to slow down the release of antibiotics (ofloxacin) from PP fibres, the biodegradable polymer layer acting as a matrix for the antibiotics,[204] but having several limitations, such as the potential interactions of the drug solutions with the coating polymer layer.

In a step forward, surgical meshes based on synthetic fibers aimed for hernia-repair have been described using only dry plasma processes in their design employing a first step for cleaning and activating the fibre surface, and a second polymerization step.[57a, 205] Commercial PP and PP/PTFE bi-component meshes were surface functionalized to confer adhesive properties using polyacrylic acid synthesized by plasma polymerization for the coating of the fibres but the antibacterial properties were conferred through a wet process incorporating silver nanoparticles.[205] In a slightly different approach, implantable PP surgical meshes loaded with antibiotics (ampicillin) were developed by a combination of plasma processes to reduce/avoid post-operatory infections; a first atmospheric plasma surface functionalization of the PP meshes focused on increasing the loading of ampicillin, and a subsequent low-pressure plasma polymerization with a thin PEG-like layer allowed conferring antifouling properties, preserving antibacterial activity and cell adhesion.[57a] In a similar approach, electrospun mats loaded with ciclodextrin complexes with an antifungal drug (fluconazole), were coated with hexamethyl disiloxane (HMDSO). The coating was able to delay the burst release of the drug from 20 min to nearly 3h.[206] Nevertheless, modulation of drug elution could still be improved on the textiles, as has successfully been achieved by plasma polymer multilayer coatings on flat substrates by the team of Arefi-Khonsari.[207] Multilayer biodegradable PCL-co-PEG (poly (ε-caprolactone)-poly (ethylene glycol) copolymer) coatings were developed on model surfaces for the controlled delivery of cisplatin, an anticancer drug[207a] which have shown excellent *in vivo* behaviour.[207b] The resulting multilayer coatings can be tailored in such a way to have controlled cell-surface interactions and are a promising approach to obtain barrier layer dependent release which may be extrapolated to coating of textiles and would be of interest to evaluate in future.

Accordingly, coating of the textile fibres by plasma polymerization seems to be one of the most promising tools to achieve textile-based drug delivery systems that are able to provide a proper drug delivery dose and rate, in which the modulation of the release kinetics of the active principle could be governed for example by the thickness and degree of cross-linking of the coating layer obtained by plasma polymerization. Current works of plasma polymerized textiles (i.e. with antibiotics) display burst release in a timeframe of a few hours, so it is expected that in the next 5-10 years research will move towards delaying this release up to a period of 2-3 weeks.

In the area of topical delivery, for instance of cosmeto-textiles discussed before, there is an apparent contradiction in the requirements: on the one hand, a suitable drug delivery rate is desired, while wash resistance would also be a clear asset for textiles which should exert their cosmetic action many times. In this case, one possible strategy would be to produce multiple barriers by plasma, which following one cycle of drug release, allowed removal of one protective layer by washing and exposing the subsequent layer of drug. Though simple from a theoretical point of view, this might be complicated to achieve. One last challenge for implantable textiles and devices incorporating drugs is not only of practical nature but rather of a regulatory nature, as incorporating drugs into their structure may change their category from medical devices to drugs, and therefore bringing them to the market can pose additional burden.

Table 2: Implantable medical textiles, with potential for being designed as drug delivery systems by plasma processes.

Product application	Type of fibre
Sutures	
Biodegradable	Collagen, polylactide, polyglycolyde
Non-Biodegradable	PA, PES, Teflon®, PP, polyethylene
Soft tissue implants	
Artificial tendon	Teflon®, PES, PA, polyethylene, silk
Artificial ligaments	PES, carbon
Artificial cartilage	Low-density polyethylene
Artificial skin	Chitin
Eye contact lenses, artificial cornea	Polymethyl methacrylate, silicone, collagen
Hernia repair mesh	PP, Teflon®
Orthopedic implants	
Artificial joints / bones	Silicon, polyacetal, PA, polyethylene
Cardiovascular implants	
Artificial blood vessels	PES, Teflon®
Heart valves	PES

3.4 Advanced fertilizer delivery

In the agricultural field the improvement of nutrient use efficiency (NUE), defined as the ratio between the amount of nutrients taken up from the soil by plants and crops within a certain period of time and that applied during that same period of time, has been a relevant issue for decades and has fostered the development of new fertilization strategies and products. As an example, nitrogen, one of the most relevant nutrients provided by a fertilizer, can be lost to processes such as leaching, ammonia volatilization or by being tied up by microbes, leading to an inefficient use of the fertilizer and to environmental concerns. A possible strategy to overcome this issue is applying the fertilizer during plant growth in several split applications, so providing a sigmoidal pattern of nutrient supply that better matches the plant demand; on the downside, this strategy is clearly labour-intensive and strongly dependent on weather conditions.

An alternative strategy is to use enhanced efficiency fertilizers (EEFs) which are a broad family of products tied together by a common idea: improving the NUE and lowering the environmental impact and the labour cost associated with the use of the fertilizer by controlling the release of nutrients and matching it to the plant demand over time.[208] Among EEFs, the most common products are encapsulated solid fertilizers:

conventional fertilizer materials encapsulated by a protective coating responsible for controlling water penetration and thus the dissolution rate, the nutrient release and its duration; these coatings may be water insoluble, semi-permeable or impermeable but porous and can be divided in to three main groups depending on the coating material: sulphur coatings, polymeric coatings or a combination of the two.[209] Sulphur coatings, still the most widespread due to their simplicity and relatively low cost, offer an impermeable membrane that slowly degrades through microbial, chemical and physical processes. The nutrient release rate varies with the thickness of the coating and is strongly affected by its quality, as the presence of micropores and imperfections severely hamper the coating efficiency and lead to undesired bursts in nutrient release. By contrast, the nutrient release through the more expensive polymeric coatings is less affected by soil pH, salinity, texture, microbial activity and redox-potential, thus enabling a more predictable nutrient release rate and the possibility to define more efficient fertilization strategies. These characteristics are leading to an increasing use of polymeric coated fertilizers, which are bound to surpass the diffusion of sulphur coated ones. Finally, combined sulphur and polymeric coatings have intermediate properties and costs.

Polymer coated fertilizers promise significant benefits in terms of crop yield increases, management flexibility, reduced labour costs and environmental issues, yet production costs have limited their use in large-scale production of commodity crops (e.g. corn, wheat); indeed, due to the cost of current polymer mixtures and production processes, polymer coated fertilizer may be between 4 to 8 times more expensive than corresponding conventional fertilizers,[210] thus their main application has been limited to high-value crops (e.g. vegetables, nurseries and seed production).

The world fertilizer market with about 190 million tonnes of use forecast in 2017/2018 (IFA May 2013) presents enormous potential for plasma technology. The development of less expensive polymer materials and production process is clearly an essential step to increase the diffusion of polymer coated fertilizers, but two other aspects need to be improved as well: the degradability of the coatings, to avoid the persistence in the soil of the synthetic encapsulating materials, and the comprehension of the mechanisms governing the nutrient release from the coatings and their correlation with the physicochemical and morphological properties of the coatings themselves.

3.5 Optoelectronic materials and structures

Plasma-enhanced chemical vapour deposition of thin polymer films and multi-layer structures is well-established and remains a highly-active area of investigation. As a solvent-free, vapour-phase technique, where monomer vapours assemble into polymeric films directly on the surface of a substrate via free-radical polymerization, PECVD combines process flexibility, low-temperature processing, and conformal coverage of films with high chemical purity and a high degree of uniformity over a large area with practically no surface or substrate restrictions.

Given that most organic or oxide channel layers in field effect transistors (FETs) can be readily damaged by high-temperature or solvent-based deposition processes typically used for fabrication of inorganic insulators and insulating polymers, respectively, the dry, mild conditions of PECVD make this process particularly attractive.[211] Being virtually substrate-independent, PECVD deposition of polymer onto hydrophobic surface of graphene may produce films that are thinner and more uniform in comparison with solvent-based deposition, providing a more facile method for fabrication of graphene transistors. FETs incorporating polymer/graphene instead of inorganic/graphene channel interfaces have been shown to have better performance due to lower surface phonon scattering.[212]

Another highly attractive feature that has been recently exploited is the ability of PECVD to produce high quality, optically-transparent thin films from chemically-heterogeneous precursors. Where conventional

polymer synthesis demands chemically-pure, high cost input materials, minimally-processed natural products can significantly lower the economic and environmental costs of polymer production without compromising the performance of thus-produced materials in optoelectronic applications.[213] Furthermore, there is an opportunity to produce coatings that combine optical and charge transport properties, controlled degradation profile, and attractive biological activity. For instance, PECVD-produced polymers from naturally-occurring terpinene-4-ol are biocompatible, possess bactericidal activity against a wide range of pathogenic bacteria, are mechanically-flexible, optically transparent and display hole-transporting electron-blocking behaviour, the latter being a highly desired feature to control the movement of charges in devices such as light emitting diodes (LEDs).[214] These properties align well with the demands placed on implantable and corporeal optoelectronic materials.

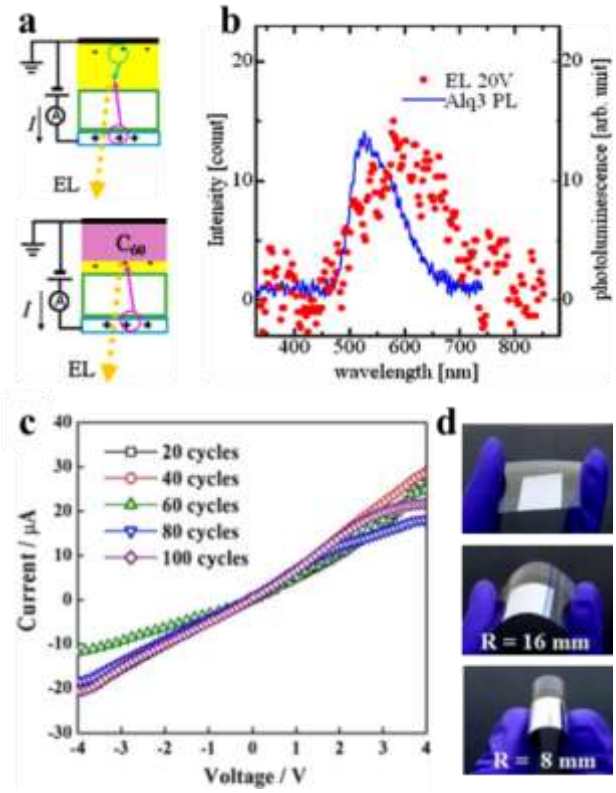

Figure 19. (a) The electron-blocking hole-transporting property of polyterpenol controls charge transport in organic electronic devices (green layer polyterpenol, yellow layer Alq2, black layer Al, blue layer IZO). (b) Electromagnetic radiation as a result of electron–hole recombination at Alq3 layer in devices with polyterpenol charge transport layer. (c) I–V characteristics of the hybrid flexible photodetector with 185 nm photoactive plasma-polymerised polyaniline–TiO_2 nanocomposite layer under 365 nm UV illumination at 3.25 mW/cm^2 intensity after 20–100 cycles of bending. (d) Images of the flexible polyaniline–TiO_2–based hybrid device under different bending states. (a, b) reproduced with permission from.[214a] (c, d) reproduced with permission from [215].

Despite the significant amount of progress made in understanding the mechanisms of, and ability to control plasma-enabled polymer assembly, a number of issues endure. In many applications, the use of even moderate vacuum has the potential to restrict both scalability and compatibility of PECVD with high-throughput manufacturing, such as roll-to-roll processing, for which atmospheric pressure plasma (APP) polymerisation may eventually become a more suitable option for continuing processing. However, it should be noted that there are a number of successful examples of the use of roll-to-roll processing at reduced pressure. These systems are characterized by high cost- and material-efficiency, and excellent quality of thus-produced materials and structures, the features that may not be readily

attainable using currently-available APP technologies. Whilst most conventional APP jets have insufficient plasma energy in ambient air to activate the monomer and induce polymerisation, there are jet array devices capable of imparting sufficient particle energy to sustain fragmentation and recombination processes.[74a]

Where plasma APP processes offer considerable advantages is in the deposition of optoelectronic devices on surfaces of flexible objects with complex topography without the need for a complex processing environment. Here, APP enabled site-specific delivery of polymer building blocks to enable defect-free, uniform coating, as well as facilitate the deposition of polymer-based composite materials. At low pressure, plasma has successfully been used to fabricate UV sensitive, mechanically-flexible hybrid photodetector films based on an aniline–titanium dioxide nanocomposite, characterised by high photoconductive gain ($G = 4.56 \times 10^4$) and high responsivity ($R = 9.36 \times 10^3$ AW^{-1}) at 254 nm, and good folding strength and stability.[215] Devices based on PECVD-deposited emissive layers based on conjugated polymer films, e.g. naphthalenes, displayed broadband electroluminescence (centred at 535–550 nm) and photoluminescence, with spectra dependent on the plasma process conditions.[216] At atmospheric pressure, plasma deposition of an aerosol of the colloid produced thin films of nanotubes with good conductivity,[217] suggesting that it may be possible to deposit composite coatings following a similar approach. Plasma etching can also be used to selectively remove the carbonised top polymer layer of composite layers and expose the underlying filler of the composite films to enhance their electrical performance.[218]

Trade-offs between film quality and area of coverage and deposition rate remains an area of concern. Spatio-temporal control of chemical species and their distribution of density and phases remain a challenge, more so in APP than in PECVD, with the resulting films characterised by substantial surface roughness. Where gas phase processes depend on the energy per molecule and result in the formation of comparable reactive chemistries in APP and PECVD, precursor molecules will be subject to orders-of-magnitude more collisions while traversing the glow region in APP, leading to markedly different surface processes, and thus affecting chemical, mechanical and morphological characteristics of the films.[219] These properties can have significant implications for the optical transparency or conductivity of thin films, such as polyaniline and polythiophene.[74a, 220]

To effectively predict and control the deposition and assembly of thin films on objects with complex topographies it is essential to understand the mechanisms that govern chemical and physical gas and surface interactions in atmospheric pressure plasma processes. This is not trivial and demands diagnostic techniques capable of capturing relevant process information without significant disruption of the reaction field with high spatio-temporal resolution. Realisation of these goals also demands complex models that can capture processes from macro- to nano- and atomic- scales.

3.6 Flexible electronics

The term “flexible electronics” refers to electronic devices that can be bent, folded, stretched, or conformed regardless of their material composition without losing functionality. Unlike conventional electronic devices which are limited to rigid substrates, flexible electronic devices will be applied to inherently non-rigid substrates such as plastics, paper, fibres, and even biological tissues. These flexible devices enable new ultra-lightweight applications, ranging from sustainable energy to smart sensors and bioelectronics. Examples of these are energy-efficient, flexible lighting, lightweight photovoltaics, stretchable sensors and dissolvable electronic implants.

Low temperature processing is required to fabricate flexible electronics. The active components may be organic conductors and semiconductors and the substrates themselves will be unstable at elevated temperatures. High speed – low cost production will drive the development of atmospheric pressure, roll-to-roll processes. A key factor in these advances will be plasma technology. Plasmas allow material processing to take place at low temperatures since the energy is supplied by energetic particles in the plasma rather than thermal energy. Plasmas also afford a much greater degree of control over precisely where the energy is applied, the amount of energy which is applied and the physical and chemical processes which it can activate. This section summarises some of the challenges and opportunities in plasma processing for flexible electronics.

Many of the proposed applications require *polymeric substrates*. Materials such as polymethylmethacrylate (PMMA), polymethyldisiloxane (PMDS), polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) have been proposed as substrate materials.[221] In particular, PDMS is a flexible, stretchable, and transparent material that has been studied and intensively developed for a wide range of applications including microfluidics, microelectromechanical systems, biological sensors, and stretchable displays for advanced electronics.[222] The adhesion of the active material layer to the polymer is critical. They are low surface energy materials and the bonding between the deposited material and the polymer is generally poor. Oxidation of the surface in an oxidizing atmosphere is an effective way of increasing its surface energy and improving adhesion. Another option is grafting of hydrophilic groups on to the polymer surface. Plasma activation or plasma grafting, particularly atmospheric pressure (AP) plasma is the preferred way of doing this given the need for low-cost production. For AP processes, there are three main categories: plasma jets, corona discharges (CDs) and dielectric barrier discharges (DBDs). They allow both plasma oxidation and plasma grafting by the incorporation of a volatile precursor in the gas stream. Plasma jets are small area sources which brings advantages and disadvantages. They allow a degree of relatively crude patterning by localized treatment but they are not efficient for uniform, large area processing. For this, some form of extended source is necessary. The main large sources are CDs and DBDs, CDs are simple to operate but suffer from the fact that the plasma is not uniform and arcs and streamers occur which can cause pitting and degradation in the polymer.[223] DBDs give a more uniform plasma but still suffer from filamentary discharges to a degree which depends on the electrode separation. The operation of all these plasma systems is dependent on the gas mixture used. Typically, plasma is stabilised by an inert gas such as Ar or He which can be used as a carrier for the oxidant with He being the most effective. This brings much increased costs, particularly in the case of He. The Diffuse Coplanar Surface Barrier Discharge (DCSBD) is a large area plasma system which avoids the formation of filamentary discharges, even with discharges in air, water vapour or other reactive gas mixtures.[224] However, further work is necessary to increase the effective speed, increase the discharge area and further characterize these types of plasma system for efficient incorporation into polymer processing.

Active layers. The necessary materials are semiconductors, conductors and insulators and photonic structures. These must be deposited and patterned in methods which are compatible with polymer substrates. The goal for low-cost production is AP or sub-AP, roll-to-roll technology. To achieve this, low-temperature chemical vapour deposition (CVD) or even solution growth will be necessary. For CVD, plasma processes will need to achieve a low enough deposition temperature.[225] In particular, atomic layer deposition (ALD, also known as molecular layering (ML)) can produce highly controlled, low temperature deposition processes for active materials even at AP.[226] In ALD, plasma processes add flexibility to the processes which can be used and the lower temperature limits which can be achieved. These processes are called plasma-enhanced ALD (PE-ALD). Recent work on this topic has shown that roll-to-roll deposition is possible with ALD. High structural quality is needed for these active materials. This can be a challenge for AP processes. With AP CVD processes it is difficult to achieve

homogeneous layers; however, with PE-ALD these are much more feasible, even at low temperature. Nevertheless, significant advances are needed in the quality of the layers. Solution-based deposition methods typically give layers of insufficient quality. Post-deposition plasma treatment is one possible way of improving the quality.[227] Plasma sintering of printed metallisation for low-cost patterned structures is an active research area [228] as is sputtering.[229]

Environmental protection layers. Flexible electronics need protection from environmental degradation. In particular, OLEDs and organic photovoltaics are extremely sensitive to moisture and require barrier layers with a water vapour transmission rate (WVTR) in the 10^{-6}g.m^{-2}.day^{-1} or better to ensure a multi-year lifetime for flexible lighting or power generation. Currently, flexible barrier layers with adequate properties are very expensive and cannot be easily integrated into a roll-to-roll process. PECVD is a process which can achieve good barriers,[230] however, the technology with probably the best prospects of achieving this is ALD. ALD barrier layers produced by a roll-to-roll process have been shown to have WVTR levels in the 10^{-6}g.m^{-2}.day^{-1} range at reduced pressure.[231] AP processes such as ALD and DBD's can also achieve high barrier levels [232] with layer thicknesses in the 10s of nm range. The processes typically use water as an oxidizer in the deposition of metal oxides in a purely chemical process. To enable faster low temperature processing of barrier layers, a plasma process using a non-water oxidizer will be necessary. The protection layer must be resistant to mechanical damage, flexing and stretching. Complex layer structures must be developed to meet these requirements while maintaining function.[233]

Table 3: Summary of needs and required breakthrough research for flexible electronics.

Element	Needs	Research required
Polymeric substrates	(1)Large scale, diffuse, atmospheric pressure and sub-atmospheric plasma sources for deposition and surface modification. (2) Use of low-cost gases to minimise running costs. (3) Improved knowledge of atmospheric pressure surface-plasma physics and chemistry	(1) Study of plasma instabilities to avoid filament formation and damage to polymers (2) Physics and chemistry of, in particular, AP plasmas. (3) Surface interactions between AP plasma and polymers. Detailed analysis of structural changes.
Active layers	(1) Improved active materials requiring improved plasma processes for AP and sub-AP roll-to-roll production for plasma enhanced CVD (PECVD) and PEALD. (2) Extended, uniform plasma sources for AP and sub-AP application. (3) Improved post-deposition plasma treatment for enhancement of material properties. (4) New active materials, such as graphene, spintronic materials, etc. and effective methods for large scale deposition.	(1) Fundamentals of PECVD and PEALD deposition processes. (2) New material development for improved conductors, semiconductors and insulators, photonic structures, spintronic materials etc. (3) System development for AP and sub-AP roll-to-roll plasma processes. (4) Plasma effects on material properties.
Environmental protection layers	(1) Low-cost ultra-barriers against water and oxygen transmission. (2) Barrier production integrated in a roll-to roll system. (3) Resistance to mechanical, damage, flexing and stretching.	(1) Plasma sources for AP and sub-AP spatial ALD processes for roll-to-roll production. (2) Development of new materials for barriers using plasma processes. (3) Increased knowledge of the effects of plasma during material deposition. (4) Influence of mechanical and environmental stress on plasma-deposited barriers.

Outlook and conclusions

In the fields of plastic and textile production, plasma science will continue to play a pivotal role over the next decade, it is foreseen that a new pillar will be formed in a couple years. Beside the enabling technologies, smart surfaces and complex coatings, it is expected that new advanced materials and structures will arise via plasma processing. These advanced materials will be likely feature in optoelectronic materials and structures, flexible electronics, fuel cells and batteries, and self-repairing materials. Some onsets have been already covered and presented in various sub-sections. Here we will deal with highly-tailored materials, which will have a targeted purpose and time span. This will, to a certain extent, also enable controlled biodegradability of coatings and polymers via plasma processing and targeted construction of certain molecules at the atomic scale.

Several strategic lessons have been learned over the past ten years:

(1) There is a need for continued, focused investment in theory, investigation methods and plasma processing at large scales, using low-cost technologies such as atmospheric pressure plasma processing, new technologies enabling high surface area treatment of non-planar substrates as well as using combined or radically new plasmas such as processing materials by plasma in liquids.
(2) More research and application of plasma for the design of smart surfaces is needed, where precise control of plasma and surface reactions is vital. Through mastery of the plasma, we will enable precise functionalization which will increase already widely used plasma for bonding, functionalisation for sensor performance and the design of environmentally-responsive polymers. Significant opportunities are offered in the area of plasma micropattering for polymeric surfaces, following very successful traditions of plasma usage in the microelectronics sector. A great frontier in plasma processing might be foreseen for 3D printing technology and electrospinning processes, giving plasmas completely new abilities in the processing of polymers and textiles.
(3) The entire field is constantly spreading and evolving, being on the sharp rise for the design of complex surface coatings. It covers everything from macromolecule grafting to the use of nanomaterials, where new applications arise almost every day. Existing technologies include antibacterial coatings, mimicking nature with biomimetic coatings, healthcare applications such as drug delivery coatings or even the large market of advance fertilizer delivery.
(4) Plasma science and technology has the potential to support sustainable development of new ecologically benign processes to preserve water resources, reduce CO_2 emissions, save energy, and other resources, efforts which can be extended over the next ten years.
(5) Besides new emerging areas, more traditional industries such as the automobile, paper, fertilizer, etc. may provide opportunities for large scale application of plasma technology.

These strategic lessons pave the way to tackle three grand challenges: (1) *Developing enabling technologies for plasma sources and processes*; (2) *Designing smart surfaces on polymers and textiles*; and (3) *Designing complex surface coatings including those with macromolecules and nanomaterials*, which will be addressed in the forthcoming 10 years. Overcomming these challenges is expected to provide at least an additional 1 to 3 billion EUR market share for the plasma processing of plastics and textiles. This will enable a permanent transition to more sustainable processing and a better, safer environment, making plasma a leading and dominant technology for the future.

Acknowledgment

This Paper is a result of the *PlasmaShape* project which was supported by funding from the *European Union Seventh Framework Programme* (FP7/2007-2013) under grant agreement n° 316216.
During this project young scientists and renowned and outstanding scientists collaborated in the development of a political-scientific consensus paper as well as six scientific, strategic white papers. In an unique format core themes such as energy, optics & glass, medicine & hygiene, aerospace & automotive, plastics & textiles, environment & agriculture and their future development were discussed regarding scientific relevant and economic impact.

We would like to thank our colleagues from 18 nations from all over the world (Australia, Belgium, Czech Republic, PR China, France, Germany, Great Britain, Italy, Japan, The Netherlands, Poland, Romania, Russia, Slovakia, Slovenia, Sweden, Switzerland and the USA) who have participated both workshops of Future in Plasma Science I and II in Greifswald in 2015/2016. The valuable contribution of all participants during the workshops, the intensive cooperation between the project partners and the comprehensive input of all working groups of Future in Plasma Science was the base for the present paper.

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Table of Contents

This white papers tries to outline the future of plasma science and technology related to plastics and textiles with the current state-of-the-art and grand challenges, which need to be addressed to move the frontier of this field. Readers will learn where we stand today, and where do we want to go in the future. It is a “navigation chart” for plasma in plastics and textiles for everyone who is interested in the field!