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Plasma Polymerization in the Design of New Materials: Looking through the Lens of Maleic Anhydride Plasma Polymers

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Abstract

Plasma polymerization is a well-established process for the deposition of thin polymeric films on various types of substrates. The potential of this technique for promoting changes of substrates wettability constitutes one of the most basic and often reported application. However, as novel technological demands emerge, and with it the range of available characterizations, plasma polymers are having their niche of applications and properties expanded. The properties of these materials are commonly tailored through the variation of the polymer chemistry, post-functionalization or other post-treatment processes. That chemical versatility allows the use of plasma polymers in adhesives, water treatment, biomedicine and many other fields. The creation of nanostructures via lithography or during the deposition process itself, constitute other dynamic fields for new plasma polymer materials. In the current review, the design of materials through plasma polymerization is addressed with the direction given by our expertise in maleic anhydride plasma polymers (MAPP). A non-exhaustive number of applications of plasma polymers is provided to non-specialists as an overview of the materials coming out from the field of this chemical-vapor deposition process. A more complete analysis of the literature on maleic anhydride plasma polymers is also performed.

Keywords: materials design, plasma polymers, maleic anhydride, functionalized polymers, surface chemistry.

1. Introduction

As the changes in energy sources get closer to become less fossil fuel dependent, future demands for greener process might include the reduction or elimination of chemical processes that are highly solvent consuming. It is in that context that plasma polymerization can broaden its competitiveness as a technique for the production of thin polymeric films. Essentially a solventless process, plasma polymerization can be used to deposit thin polymeric films on a multitude of substrates. That feature can be used to vary the surface physico-chemical properties of a substrate. Consequently, that results in the possibility of designing materials to niche applications, through improving barrier properties, changing surface wettability, varying surface functional groups and many others [1–3]. Plasma polymerization is thus a versatile technique for the development of a number of materials and in many cases it can constitute a great alternative to target issues encountered by other surface modification techniques.

The interest of a polymer is also strongly related to its chemistry and availability of functional groups. The reactivity of anhydride makes it a very interesting functional group to be incorporated to a polymeric chain, as it can allow several different strategies for post-functionalization. One commonly studied monomer/precursor for that is maleic anhydride. It is an organic compound that contains a dual functionality composed of an electron acceptor carbon-carbon double bond and a reactive anhydride group. Homopolymerization of maleic anhydride has been extensively studied and, although many synthetic routes have been explored, it generally renders low yields and/or low molecular weight polymers [4–6]. More commonly, copolymerization or grafting of maleic anhydride are selected strategies to provide anhydride functionalities to a set of different (co-)polymers [7–12]. That variety of explored chemical pathways are justified by the abundance of applications provided by the

anhydride functionalities on polymeric materials. Some examples of application fields include water treatment [13, 14], energy storage [15] and biomedicine [16–18]. The intersection among such different fields falls mainly in the reactivity of the anhydride group and the possibility of further functionalization of materials derived from that chemistry.

The afore mentioned fact that the homopolymerization of maleic anhydride in bulk is hard to achieve has motivated initial studies on its use in plasma polymerization and, since then, it has been a greatly explored research topic [19]. Beyond that, plasma co-polymerization of maleic anhydride and other precursors can improve film stability and allow a different range of processing conditions [20]. In this context, the combination of maleic anhydride chemistry with the relevance of plasma polymerization, in particular as a green surface modification process, provides a solid ground to novel materials developments. Maleic anhydride was chosen as a good example for demonstrating the materials that can be designed by plasma polymerization and evaluating its future potentials and challenges.

2. Plasma State and Plasma Polymerization

Plasma is a quasineutral gas composed of charged particles (ions and electrons) and neutral particles (atoms, molecules and radicals), which exhibits collective behavior. The concept of collective behavior is associated to the presence of electromagnetic forces, which affect the motion of the charged particles, while quasineutrality expresses the idea that the number of positive and negative particles in the plasma is approximately the same, but still the electromagnetic forces are not vanished [21]. In general, plasmas can be artificially created by exposing molecules or atoms to specific conditions, such as intense heat or via a strong electromagnetic field [22].

One of the fields in plasma research deals with its application for surface modification. Such modifications can happen through surface etching, incorporation of functional reactive groups or via deposition of a solid film as a result of active species reactions. The first two cases comprise the use of so-called non-polymerizable gases, such as oxygen (O₂), nitrogen (N₂), argon, helium or air [23]. The third involves a process in which low-molecular weight molecules (precursors) are converted into high-molecular weight molecules (polymers) via assistance of energetic plasma species such as electrons, ions and radicals, which is known as plasma polymerization [24].

The principle that better describes the events occurring during plasma polymerization is called competitive ablation and polymerization (CAP). It is a concept that relates the ablation of materials in plasma to the deposition of a solid from the plasma phase. The plasma phase contains various energetic species including ions, electrons and chemically reactive species. These energetic species are not only originated from the precursor, but also result from ablation of surfaces (reactor wall, substrate and recent deposited solid layer) through bombardment of electron beams, ion beams and VUV/UV irradiation. Hence, ablation deals with fragmentation of solids exposed to plasma, while the reaction and recombination of these species lead to the deposition of a solid polymer [25].

The complex process of plasma polymer deposition involves several distinct modes, such as: radical chain-growth polymerization, ionic chain-growth polymerization (cationic, anionic), ion-molecule reaction, precursor fragmentation followed by poly-recombination (forming randomly and irregularly structured materials), precursor conversion to polymer-forming intermediates and chemical grafting onto radical sites or functional groups on the surface [26]. The uniqueness of plasma polymers arises from these complex reaction mechanisms. As a consequence, plasma polymers are formed by crosslinked, fragmented and rearranged units from precursors, instead of repeating monomer units like conventional polymers [24].

Despite the differences in the chemical and physical properties between plasma polymers and conventional polymers, plasma polymerization process offers several advantages over conventional polymerization. For example, a broad range of precursors can be used (no need of specific reactive functionality), films are often cohesive and adherent to a variety of substrates, it is a solventless process and ultra-thin films can be generally produced. Besides, the chemical and physical properties of the plasma polymer films can be tailored through careful control of plasma polymerization conditions [27]. In other words, the adjustment of operating parameters/conditions changes the balance between ablation and polymerization, as well as the chemical composition of the plasma phase and the reactions occurring among plasma species, thus modifying the properties of the deposited plasma film.

There are several factors capable of influencing the properties of the deposited plasma film: precursor flow rate, substrate temperature, pressure of the process, sample position inside the reactor, reactor type, polymerization time and peak power are some of them [27, 28]. However, the so-called Yasuda parameter, W/FM (where W is the peak power, F is the flow rate and M is the molecular weight of the precursor), has proven to be efficient to control the chemical structure of plasma polymers, since it gives an idea of power input per precursor amount [22, 23]. Despite being a good parameter to investigate deposition kinetics and functional group retention in a given reactor, it fails to predict the results when reactors with different designs are used, since no geometric factor is taken into consideration for the estimation of this parameter. The use of a macroscopic kinetic description of the plasma polymerization and determination of apparent activation energy enables an easy strategy for optimization of the deposition process [29, 30]. Another proposed parameter that could provide a better prediction of the plasma polymerization process is the ion flux [31]. It is either directly or indirectly involved in creating radical sites for neutral species grafting and

providing mass to the growing material. The results showed that ion flux was a better predictor of deposition rate and functional group retention.

One of the major drawbacks of plasma polymerization process was the limited control over the chemistry and retention of functional groups due to high degree of fragmentation of the precursors. However, the introduction of modulated or pulsed excitation provided more versatility and allowed a better control over the physico-chemical properties of the films. In pulsed processes, the duty cycle (DC) has to be taken into account. DC is the ratio between the pulse on-time (t_{on}) and the total time of the pulse ($t_{on} + t_{off}$). During t_{on} , the excited species are produced and all reactions described before take place. After the pulse is over (t_{off}), the species can recombine and the plasma polymer is expected to be richer in functional groups and less crosslinked when compared to continuous wave deposition (Figure 1) [26].

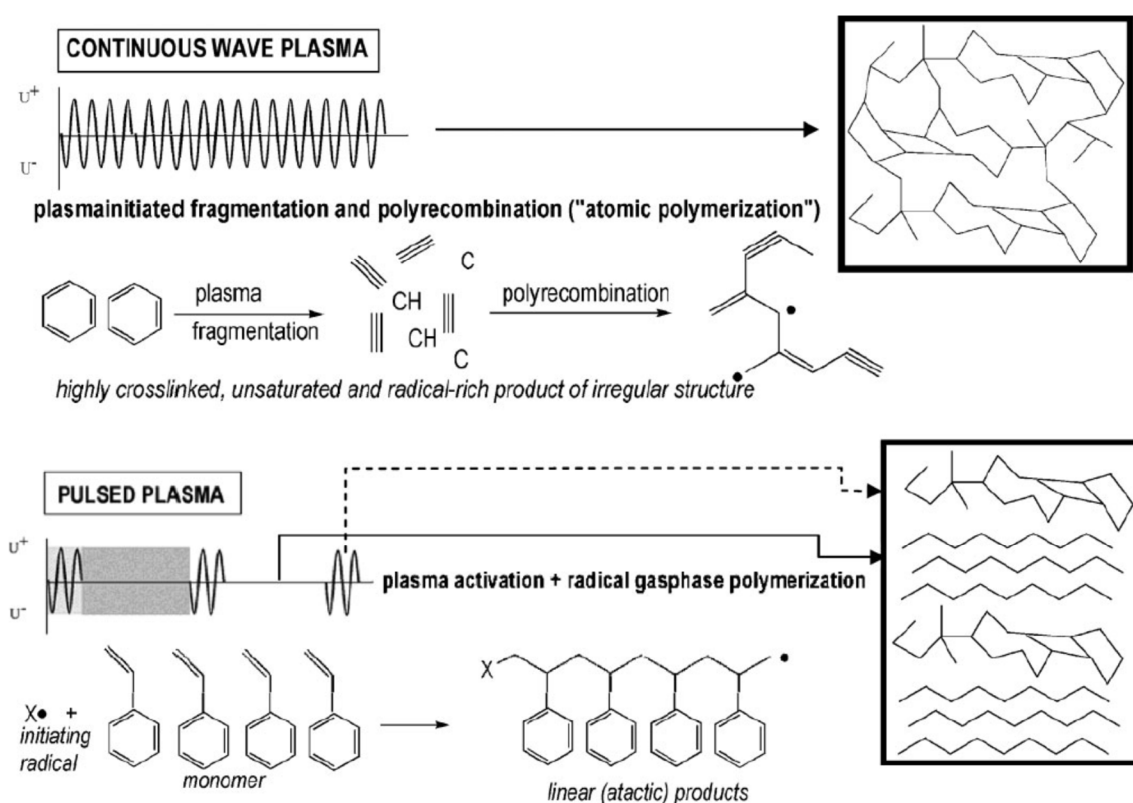


Figure 1 – Schematic representation of continuous-wave and pulsed-plasma polymerization and their products (plasma polymers). Reproduced with permission from [26]. Copyright 2011 John Wiley and Sons.

A great variety of thin films containing specific functional groups has been explored including: anhydride [19], carboxyl [32], hydroxyl [33], amine [34], cyano [35], epoxide [36]. The following section aims to exemplify, with the case of maleic anhydride, how those aspects of plasma polymerization can be driven to the production of physico-chemically diverse plasma polymers.

3. Plasma Polymerization of Maleic Anhydride: Functional *versus* Crosslinked Films

The mechanisms of plasma polymerization can be combined with the adjustment of several spatial and temporal parameters [37, 38]. They allow to control the physico-chemical properties of plasma polymers, among which the retention of functional groups and the crosslinking density can be highlighted [26, 39]. That brings a number of opportunities, as the surface can be designed according to a specific demand of a more functionalized or crosslinked polymer coating.

One of the first studies of plasma surface treatment with maleic anhydride was performed through a microwave plasma process and aimed to modify the surface of polydimethylsiloxane (PDMS) [40]. In their system, only short times of deposition were allowed, as the precursor was directly exposed to the plasma phase and degraded over longer exposition times. That limitation could be overcome with other reactors' designs. The pioneer in the use of the most commonly explored radio-frequency (RF) glow discharge of maleic anhydride was J. P. S. Badyal. In his first work with that precursor, both continuous-wave and

pulsed excitation were used in order to evaluate the functional group retention of anhydride [19]. For that, the surface chemistry was investigated under different processing conditions in which the highest retention of the anhydride functionality (28%) was favored by pulsed excitation, low average power and long t_{off} . An ideal linear chain of maleic anhydride homopolymer would have 50%.

Intending to optimize the functional retention of anhydride through pulsed plasma polymerization, Siffer *et al.* [28] proposed a chemometric approach based on screening experiments and surface response modelling. The obtained optimum condition resulted in an anhydride retention of approximately 32% (Figure 2).

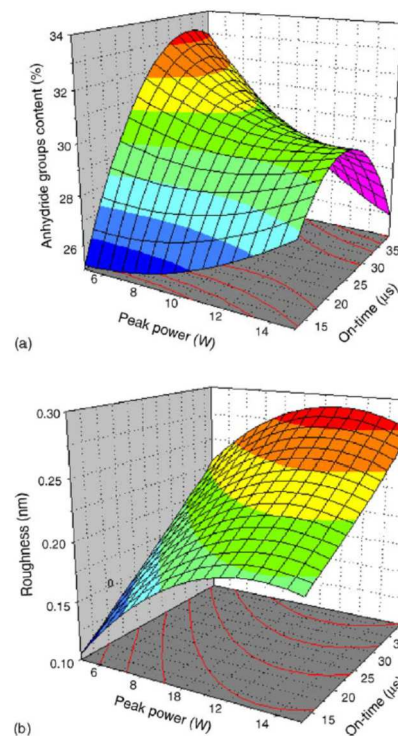


Figure 2 – Central composite strategy, response surface of: (a) maleic anhydride groups retention and (b) roughness. Reproduced with permission from [28]. Copyright 2005 Elsevier.

Later on, Mishra and McArthur [41] compared plasma polymerization of MA under continuous-wave and pulsed excitation using the same average power (1 W). It was observed that the anhydride ring content was favored by a short t_{on} and a long t_{off} . They have shown, via

mass spectrometry, that an increase in precursor fragmentation occurs for long t_{on} and short t_{off} , resulting in a lower anhydride retention in the polymer. Nevertheless, an increase in the retention of anhydride groups is accompanied by some drawbacks. It can impact the film stability, its deposition rate and its adhesion to the substrate [28, 41, 42]. Lower energy input to the system can result in less fragmentation of the precursor, decreasing crosslinking degree and creating less anchoring points with the substrate, i.e. worsening adhesion [19, 42]. Thus, the selection of the operating parameters resulting in stable, well-adhered and anhydride ring-rich film is a challenging task. However, the relatively easy possibility of functionalizing different surfaces with variable content of anhydride is one of the main advantages of plasma polymerization compared to the grafting or co-polymerization bulk strategies. Some advantages and drawbacks of plasma polymerization of maleic anhydride when compared to other selected techniques, such as grafting of functional polymers to plasma activated surfaces, UV and electron beam immobilization of functional polymer thin films and low pressure plasma immobilization, have been reported [43]. The main advantage of plasma polymerization was identified as the simplicity of the procedure with a one-step functionalization and without thin film preparation from solution that was required by some of the other approaches analyzed. It was through exploring the versatility and simplicity of plasma polymerization that many possible applications have been reported. In the next section, a focus on some properties of maleic anhydride plasma polymer is reported together with some applications that arise from them.

4. Influence of Hydrolysis and Derived Applications

The utility of a material for any desired application depends on the understanding of its most fundamental properties. The analysis of those properties for maleic anhydride plasma

polymers is the starting of this section. For instance, the hydrolysis and stability of anhydride groups is of great interest, as a detrimental factor for any application. The exposure of maleic anhydride plasma polymer to air and aqueous solution at ambient conditions suggested that the hydrolysis reaction of the anhydride is influenced by the crosslinking density of the film, being more prominent for the less crosslinked films at the same time scale [42]. The hydrolysis of maleic anhydride plasma polymers induces changes in the nature of functional groups of the films, however it does not necessarily modify the stability of the polymeric structure. Drews *et al.* [44] observed that full hydrolysis of anhydride groups could not be achieved over several days of immersion of the thin plasma polymer in water, either at room temperature or at reflux (100 °C). A similar result was obtained when the film was immersed in sulfuric acid (1 M) at room temperature for 17 hours. However, in alkaline solution (10 mM NaOH) 90% of anhydride groups were hydrolyzed in less than 15 minutes. In some of the conditions tested even dissolution of the MAPP film were observed in that medium. It was shown that both hydrolysis and stability were strongly related to the deposition conditions of plasma polymerization, generating more or less crosslinked films. However, an increase in degree of crosslinking hampers the film swelling and the access to functional groups. The reactivity of the anhydride groups was shown to provide a peculiar swelling behavior to MAPP when compared to other plasma polymers [45]. The swelling of MAPP film in humid air and in aqueous solution was studied with emphasis on the effect of pH and ionic strength [46]. For the deposition conditions selected by the authors, MAPP films exhibited a reversible swelling behavior in humid air. Similarly, increasing the pH of aqueous solution resulted in a small increase of the film thickness due to the dissociation of COOH groups into COO⁻, while the increase of salt concentration (in basic pH) caused an increase in both thickness and refractive index associated to incorporation of Na⁺ into the free volume of the polymer network. Those results were supported by an independent work on the characterization of

hydrated MAPP films [47]. That work allowed the identification of two pK_a values at 3.5 and 9.5 ascribed to the first and second deprotonation of the dicarboxylic acid groups, respectively. The authors also reported that ionic strength has a strong influence on the adhesion forces between two MAPP modified surfaces (AFM tip and PDMS), in which the cation valence of the ions used had a relevant role in increasing or reducing that force.

The last study opens up for the second discussion of this section, which concerns how the intrinsic properties of maleic anhydride plasma polymers can be translated into a number of applications. Maleic anhydride plasma polymers have shown to improve hydrophilicity of surfaces, to provide functional groups for further molecular grafting and to be suitable surfaces for layer-by-layer deposition [48]. For instance, the potential in the biomedical field has been demonstrated through the use of Ca^{2+} ions as chelating agents between the carboxylic acid functionality of MAPP and lipid bilayers [49]. A correlation between the amount of functional groups present in the film, tailored by the deposition conditions, and the lipid coverage of the surface was observed. Concerning possible water treatment applications, the prospect of MAPP for specific capture of heavy ions, such as Cd^{2+} , has also been reported (Figure 3) [50]. That selectivity was attributed to a combination of complexation flexibility of the heavy ion with intrinsic characteristics of the MAPP coating.

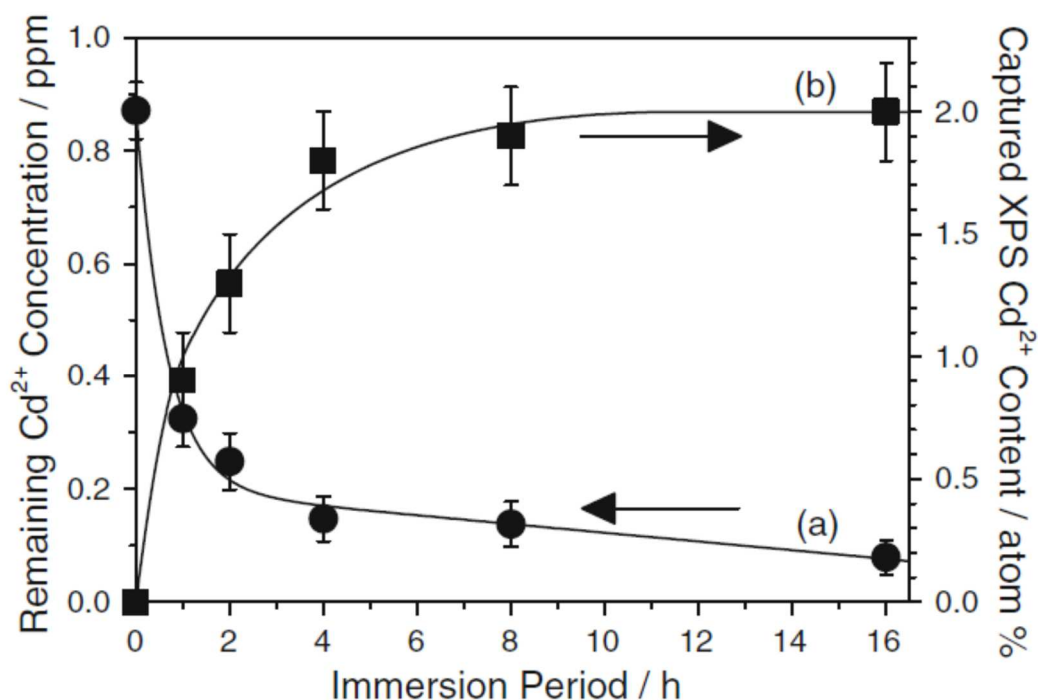


Figure 3 – (a) Concentration of $\text{Cd}^{2+}_{(\text{aq})}$ measured by atomic absorption spectroscopy of cadmium(II) chloride solutions following period of immersion of MAPP coatings; and (b) Cd^{2+} content of the coatings following immersion in cadmium(II) chloride solutions as measured by X-ray photoelectron spectroscopy. Reproduced with permission from [50]. Copyright 2013 Springer Nature.

In a similar domain, the hydrophilic character of MAPP enabled to increase the water flux through reverse osmosis membranes and maintained its overall salt rejection at short plasma duration [51]. Although not investigated in their work, the authors pointed that the formation of a negatively charged thin-film composite membrane could also strongly change the selectivity for specific cations or anions. Hydrolysis of a MAPP rich in functional groups can also provide good proton conductivity to the films. Nevertheless in some studied deposition conditions the film stability was compromised, as the crosslinking degree decreased [52].

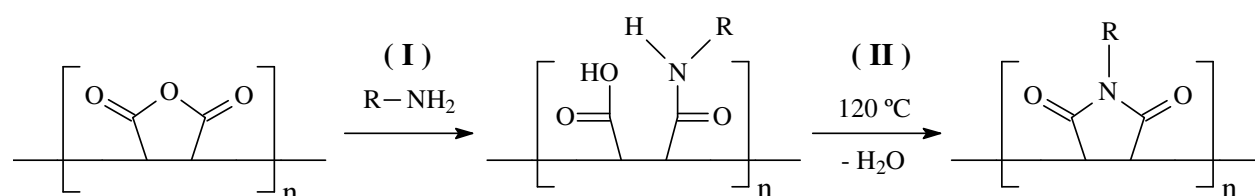
The range of prospective materials that can originate through the use of maleic anhydride plasma polymers is greatly broadened by the reactivity of the anhydride/carboxylic groups.

Some chemical methods to produce functionalized plasma polymers and several applications for them are analyzed in the following section.

5. Post-functionalization of Plasma Polymers

5.1. Single-step Post-functionalization

Chemical post-modification of (co-)polymers containing maleic anhydride is of interest for different research fields. That comes from the possibility to bring new chemical functionalities to those (co-)polymers, and consequently a new range of applications. In the case of low-pressure plasma polymerization, other functional groups could be provided by vapor phase reactions, which, besides being a green approach, can decrease side reactions. In addition, reactions with anhydride group are favored by the absence of hydrolysis competition when they are performed in vapor phase. One of the first reported derivatization reactions of maleic anhydride plasma polymers has indeed been performed in such condition [53]. In that study, post-modification of MAPP by vapor phase aminolysis was performed using two different primary amines. The reaction happened through nucleophilic attack of the amine-terminated moieties on the anhydride group producing amide and carboxylic group. An additional heating step, at 120 °C, resulted in the ring closure and the formation of cyclic imide groups (Scheme 1).



Scheme 1 – Derivatization of anhydride ring: (I) aminolysis reaction resulting in ring opening and formation of amide and carboxylic groups; (II) heating at 120 °C results in ring closure

and formation of cyclic imide group. Adapted with permission from (Evenson *et al*, 2000).
Copyright 2000 American Chemical Society.

That derivatization procedure was also used to functionalize MAPP, deposited on aluminum substrates, with allyl groups [54]. The goal was to improve the adhesion between an aluminum substrate with ethylene-co-propylene-co-diene terpolymer (EPDM) elastomers, which are quite difficult to assemble. The adhesion improvement was reached through covalent bonds between the inserted alkene from allylamine-modified MAPP and the uncured elastomer during peroxide crosslinking of the elastomer. Further studies showed that the adhesion could be tailored by adjusting the duty cycle [55]. Increasing the duty cycle resulted in less allyl functionality and higher crosslinking degree, which reduces not only the amount of reactive groups but also their accessibility for subsequent reaction with functional groups from the elastomers, resulting in decreased adhesion (Figure 4).

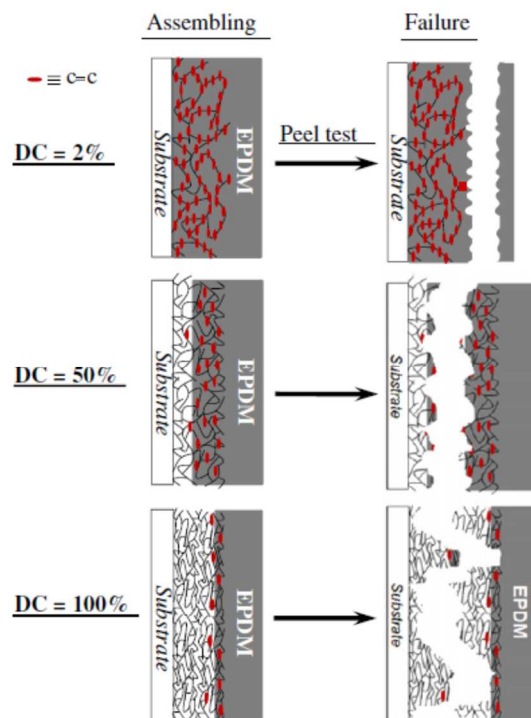


Figure 4 – Schematic representation of the effect of duty cycle in the assembling and failure modes between EPDM and MAPP treated aluminum. Reproduced with permission from [55]. Copyright 2011 Elsevier.

A later study, explored not only that approach but also a liquid phase reaction of propylene sulfide with carboxylic acids of MAPP to generate thiol functionalized thin films [56]. Functionalized films were created on the surface of carbon fibers with the goal of improving its adhesion strength to an acrylate matrix cured by electron beam. The results were compared to other approaches not based on plasma polymerization and the advantages promoted by the presence of a plasma polymer at the surface of fibers, as higher grafting of functional groups for example, were demonstrated. Such optimal polymeric interphase, covalently bonded to both fiber and matrix, led to good mechanical properties in composites cured by electron beam. Those literatures exemplify well the possible applications of functionalized MAPP as adhesive nano-layers.

Another functionalization of MAPP films encompasses the direct reaction with amine-terminated biomolecules, such as proteins and peptides, with potential application in the biomedical field [57]. An example is the irreversible attachment of bovine serum albumin [58]. The attachment of that protein was verified by subsequent binding with an antibody and evidenced by surface plasmon resonance (SPR) [59]. The effect of the duty cycle used during plasma polymerization of maleic anhydride on the degree of protein attachment was demonstrated, confirming the influence of the plasma conditions on the chemistry of the film. Also aiming a biomedical application, giant unilamellar vesicles containing an encapsulated antimicrobial were attached to MAPP thin films [60]. The goal was that the vesicles would selectively release the antimicrobial agent when in contact with pathogenic bacteria, through its lysis. In that case, the chemistry of the plasma was selected to promote an unspecific

adhesion between the substrate and the vesicles. More recently, plasma polymerization of maleic anhydride and acetylene at atmospheric pressure was used to modify biodegradable polycaprolactone (PCL) nanofibers [61]. The goal was to attach gentamicin, an antibiotic, on the coated fibers either through the generation of amides (catalyzed with N,N'-Dicyclohexylcarbodiimide) or via ionic bonding of ammonium and carboxylate groups. It was shown that both procedures generated surfaces with strong antibacterial effects. An improvement of cell adhesion (IAR-2) was observed after MAPP deposition, when compared to untreated PCL nanofibers. Cell attachment and spreading was further increased after gentamicin immobilization (Figure 5). Interestingly, the ionic bonding method resulted in surfaces with higher biocompatibility when compared to the covalently bonded gentamicin, possibly due to the absence of residual catalyst.

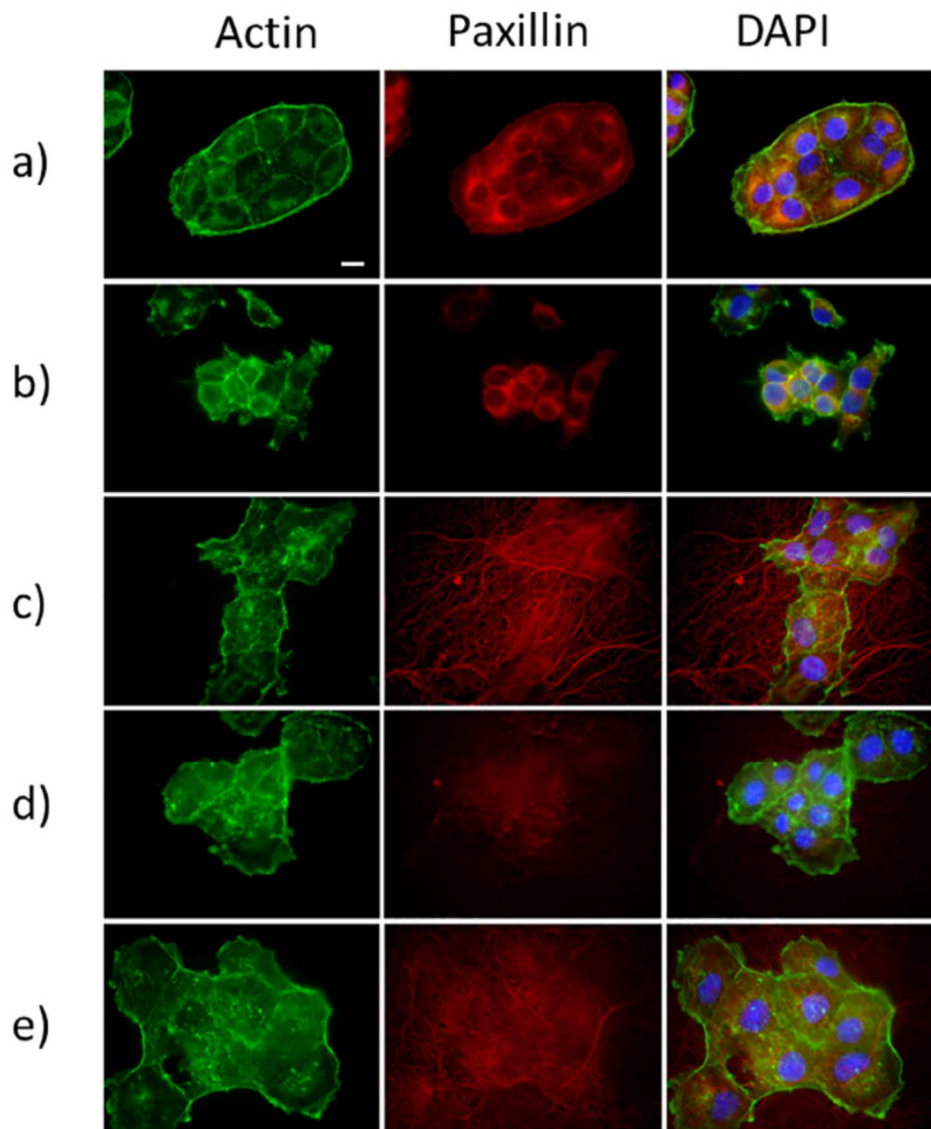


Figure 5 - Adhesion of IAR-2 cells to the surface of different substrates. Glass coverslip (a), untreated PCL nanofibers (b), MAPP modified PCL nanofibers (PCL-MA) (c), PCL-MA after ionic bonding of gentamicin (d) and PCL-MA after covalent bonding of gentamicin (e). The actin cytoskeleton and cell nuclei are stained with Alexa 488 phalloidin (green) and DAPI (blue), respectively. Bar is 10 μm . Reproduced with permission from [61]. Copyright 2018 Elsevier.

Some applications of plasma polymers are highly dependent on the nature of the substrate on which they are deposited. For instance, the reaction of hydrated MAPP with amine-

functionalized poly(ethylene glycol) (amine-PEG) was performed on poly(dimethylsiloxane) (PDMS) [62]. This allowed the development of a mechanically responsive surface, in which the control of protein adsorption was triggered by elongation of the substrate. The stretched substrate provided areas with decreased PEG surface coverage, allowing protein adsorption to happen. In another study, the functionalization of stretched MAPP coated PDMS with PEG, biotin or a peptide was used to generate a reversible chemo- and cyto-mechanoresponsive substrate [63]. By stretching the substrate, the ligands were not anymore hindered by the PEG coating but exposed and available to interact with proteinic receptors. The return of the substrate to the non-stretched state masked the ligands and expelled the receptors.

In addition to the exploitation of their initial functionality, the possibility of modifying functional plasma polymers via a multistep approach opens a large number of chemical reactions and considerably increases the diversity of the final functional groups present at the surface of the plasma polymer. However, to remain realistic and transferable to larger scale production, a multistep chemical modification procedure has to stay relatively simple, well-controllable and efficient (high yield) to justify its use. In the following section we highlight some procedures based on click chemistry, which generally fulfills well the criteria of efficiency and of reaction straightforwardness.

5.2. Multistep Post-Functionalization of Plasma Polymers: A focus on Click

Chemistry

The direct chemical modification of MAPP is restricted by the feasible reactions with anhydride/carboxylic groups and to a lower extend any residual olefin. However, that reactivity spectra can be considerably broadened by the inception of other functional groups to the surface after a first modification step. The introduction of moieties able to undergo

reactions in a relatively simple and effective way is of significant interest for materials design. In that direction, the use of click chemistry in materials science has been the subject of great scrutiny by that scientific community in recent years [64, 65].

Among click chemistry reactions, the Diels-Alder reaction has been thoroughly studied [66, 67]. Depending on the selected reactive pair, the Diels-Alder reaction offer the possibility of relatively low-temperature reaction reversibility, making it very interesting for the development of smart thermoresponsive materials [68]. The capability of applying the Diels-Alder reaction to MAPP was first successfully demonstrated by Roucoules et al. [69]. They reported a two-step process. The first step consisted in the reaction of the anhydride ring with allylamine; then it was followed by the cycloaddition reaction (Diels-Alder) of the grafted dienophile with 1,3-cyclohexadiene. That reaction proceeded with the generation of a mixture of *endo*- and *exo*-adducts on the surface (Figure 6).

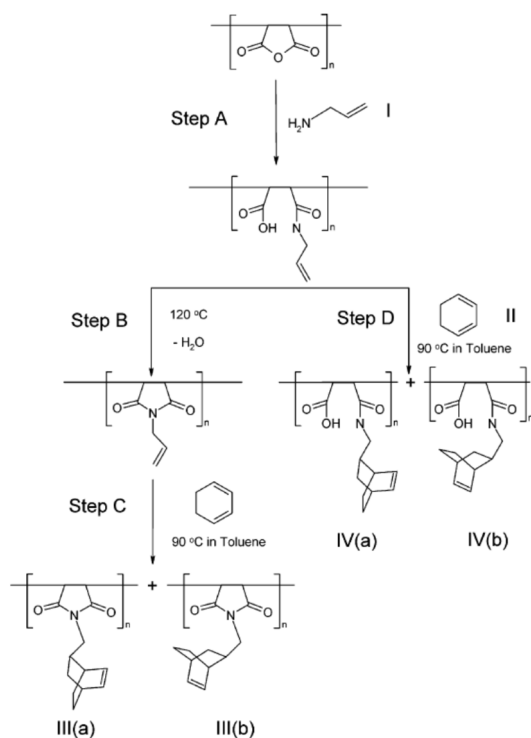


Figure 6 – Schematic representation of MAPP reaction with allylamine and 1,3-cyclohexadiene. Reprinted with permission from [69]. Copyright 2005 American Chemical Society.

Our research group has also functionalized MAPP surfaces with diene (furan) moieties and evaluated the reaction kinetics of those surfaces with a selected dienophile [70]. The reactivity of the surface was discussed in relation to its crosslinking degree and density of functional groups. The accessibility of furan groups was shown to have an impact on the reactivity of the studied interfacial Diels-Alder reaction. That result led to further studies in which the role of a spacer on that reactivity was highlighted [71]. Those publications bring interesting discussions about interfacial Diels-Alder reaction, such as confinement effects and limited mobility close to the surface, opening up an exploratory route for controlled immobilization of biomolecules on functionalized MAPP surfaces.

Huisgen cycloaddition was described by Sharpless group as the “most useful and reliable” cycloaddition [72]. As the copper-catalyzed azide-alkyne Huisgen cycloaddition allowed a more selective synthesis than the non-catalyzed reaction, it became the most explored click chemistry reaction [64]. It has also been used after a microwave-assisted plasma functionalization of polymeric substrates with maleic anhydride [73]. That procedure provided the surface with carboxylic functional groups and subsequent reaction steps of the carboxylic groups lead to the formation of an alkyne functionalized surface. That surface was used to “click” azide modified ampicillin. The antibacterial activity of the surfaces after the antibiotic attachment was demonstrated (Figure 7). Although not analyzed in the work, the advantage of such surface, when compared to the simpler approaches of antibiotic attachment already described, could be the stability and specificity of the chemistry. That fact could

potentially allow the production of more stable surfaces or the targeting of a desired molecule in a medium.

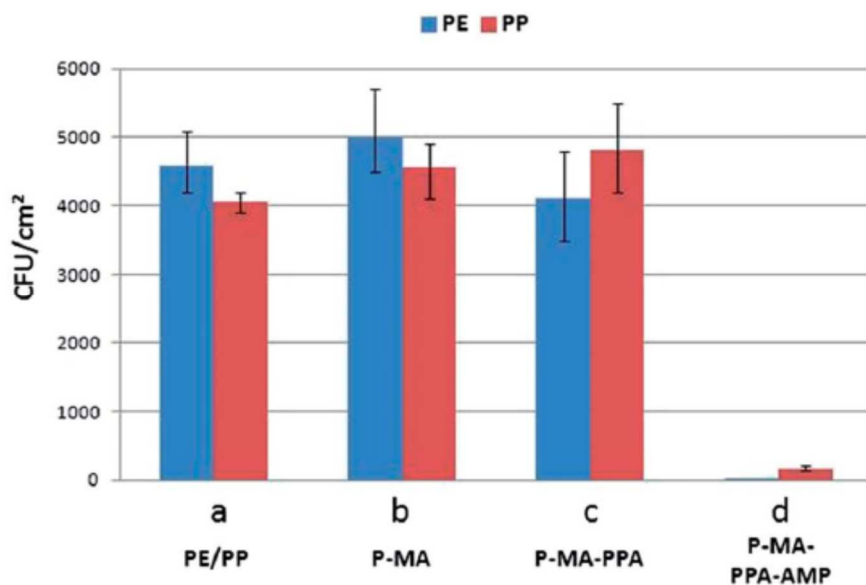


Figure 7 – Antimicrobial activity against *S. aureus* of (a) polyethylene (PE) and polypropylene (PP) surfaces; (b) PE and PP after MAPP deposition (P-MA); (c) P-MA after alkyne functionalization (P-MA-PPA) and (d) P-MA-PPA after Huisgen cycloaddition with azide modified ampicillin. Reproduced with permission from [73]. Copyright 2014 Royal Society of Chemistry.

If the number of functionalization steps could be seen as a limitation in the use of a broad range of chemistries, alternatively plasma polymerization provides the possibility of generating a multifunctional material in a single step via copolymerization. That aspect will be discussed in the following section.

6. Copolymerization

The chemical derivatization constitutes a major method for the functionalization of plasma polymers. In a different direction, it is also possible that the chemical and physical properties of the final plasma polymer could be tailored through the copolymerization of different precursors. The complexity of plasma polymerization mechanisms increases in such system, but they have been the subject of great interest [74, 75]. For instance, the copolymerization of maleic anhydride and 1,2-(methylenedioxy)benzene (MDOB) has been performed with the goal of improving the stability of maleic anhydride thin films while preserving its functional groups in a hydrocarbon matrix [76]. That surface was further reacted with polyethylenimine to create amine rich surfaces, followed by the grafting of linear methoxy-terminated polyethylene glycol aldehyde (mPEG). The ultimate goal of those functionalization steps was to inhibit protein adsorption on the modified substrate. However, the authors observed that the plasma polymer doubled the amount of fibrinogen adsorbed when compared to the native substrate, which suggested that the protein was able to diffuse into the plasma polymer. The amount of adsorbed protein decreased with each functionalization step. In a following study with the same precursors, the authors suggested that a gel-like structure was formed during the copolymerization [77]. They further showed that, after mPEG grafting, a clear reduction of cell adhesion occurred.

Besides, the deposition of a copolymer of maleic anhydride and acetylene has been used to increase functional groups on carbon nanotubes and thus enhance its sensor response to ammonia [78]. The sensor response increased almost three times compared to the untreated one, that is justified by the generation of an oxygen-rich surface that is able to adsorb more ammonia. In another study with the same precursors, XPS depth profiling allowed to discuss the effect of the molecule size on the homogeneity of derivatization with organofluorines, which resulted in different permeation of the tested molecules and evidenced the limitation of derivatization according to the selected molecule [79]. Another study also took advantage of

plasma-assisted copolymerization of maleic anhydride and acetylene to demonstrate the potential of that coating in label-free immunosensing [80]. For that, the chemistry of the films was initially assessed and the stability of the coatings in a buffer phosphate solution could be improved when samples were stored in air for a certain time before immersion in the solution. A level of detection of the antigen comparable to the ones obtained from conventionally used self-assembled monolayers could be achieved. A lower level of response could be attributed to the random distribution of functional groups and smaller surface area when compared to a 3D sensor (Figure 8).

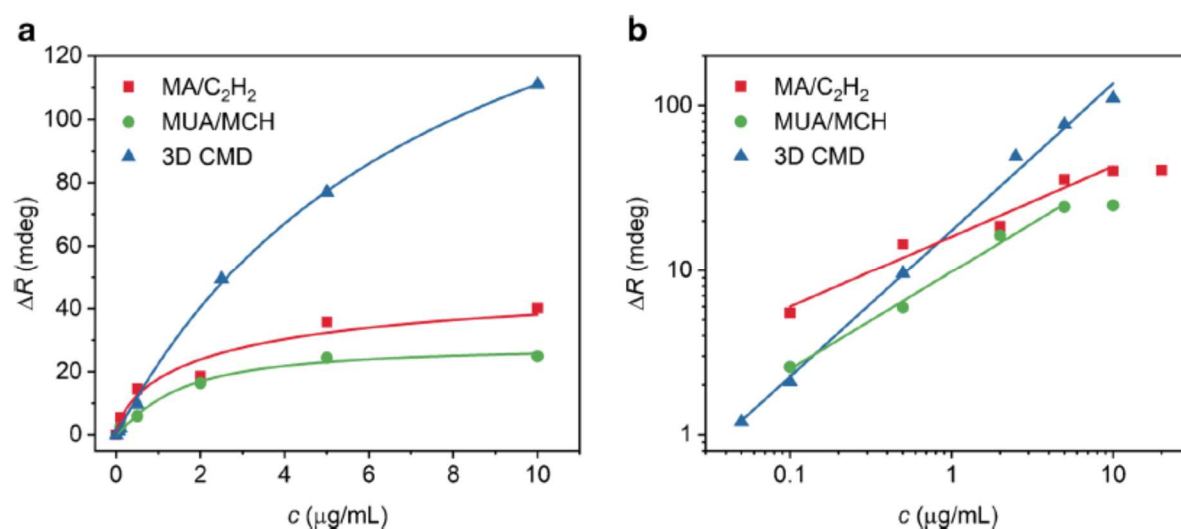


Figure 8 – Comparison of the obtained signals for human serum albumin (HAS) detection using surfaces based on maleic anhydride and acetylene plasma polymers (MA/C₂H₂), self-assembled monolayer of mercaptoundecanoic acid and mercaptohexanol (MUA/MCH) and 3D carboxymethylated dextran (3D CMD). (a) Linear scale fitted by the Langmuir model and (b) double-logarithmic plot fitted by line. Reproduced with permission from [80]. Copyright 2019 Springer Nature.

The copolymerization strategy can be used to solve limitations encountered with a specific precursor. In the case of maleic anhydride, it has been mainly used for providing better

stability to the films. Another relevant aspect that can be explored for thin coatings is their integration to other classes of materials, generating nanocomposites.

7. Nanocomposites

Nanocomposites are materials consisting of a matrix phase and an uncontinuous reinforcement which presents at least one of its dimension in the nanoscale [81]. The unique properties of nanocomposites can be partially attributed to their surface area/volume ratio, which has an impact on the phases interface interactions [82]. Plasma polymers can also be used in combination with other nanometric scale materials to create nanocomposites. The peculiarity of those systems lies on the fact that all phases are in the nanoscale, resulting in an interesting explorative field. For instance, the co-deposition of maleic anhydride and cellulose nanocrystals (CNCs) has been tested by *Samyn et al.* [83]. Cellulose nanocrystals are rod-like bio-based nanoparticles that have established applications in nanocomposites [84]. The precursors mixture was used for the deposition under different conditions of power, duty cycle, pressure and position inside the plasma reactor. The synthesized films exhibited variable patterns depending on the applied conditions. Such differences were ascribed to the metastable nature of the viscoelastic polymer film. Further work focused on a specific deposition condition, but with different concentrations of CNCs in the precursor tube, showing that the concentration of the CNCs influenced the stability of the film [85]. For the low concentration of CNCs the film was unstable and completely shrunk with the completion of the deposition; in the other hand, a metastable wrinkled-film was obtained for the highest concentration of CNCs. Also, an innovative approach for the development of patterned CNC model surfaces were established based on spin-coating process [86]. CNCs were spin-coated on a hydrophobic silicon wafer patterned with circular hydrophilic micro-domains. That

allowed the preparation of CNCs coated surfaces with different distributions: (a) a submonolayer of CNCs homogeneously distributed and (b) CNCs islands on a patterned substrate. Plasma polymerization of maleic anhydride on the latter revealed that the presence of CNCs could act as nucleation points for the formation of complexes structures (Figure 9).

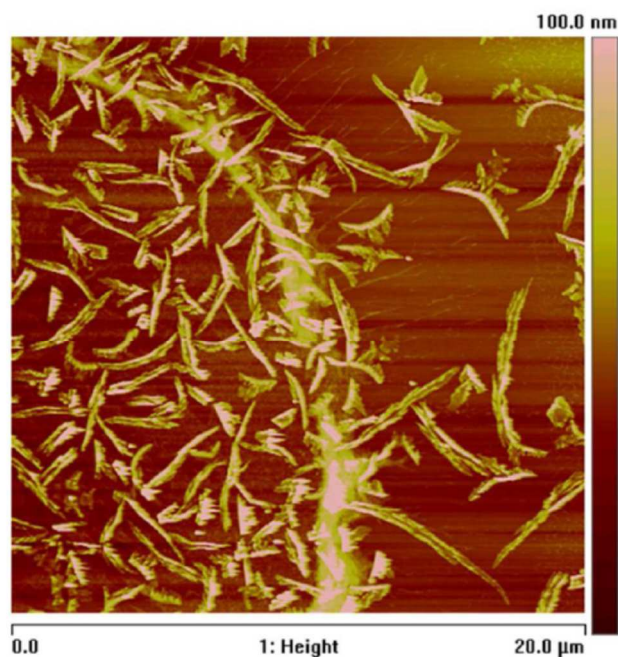


Figure 9 – Height AFM images of MAPP deposited over a patterned substrate containing islands of high density of CNCs. Reprinted with permission from [86]. Copyright 2015 American Chemical Society.

Surface treatment of bare silicon wafer and the addition of CNCs affected the stability of the MAPP films obtained at low duty cycle [87]. The formation of blister was observed as a consequence of swelling-induced stress relaxation, and at low concentration, the CNCs could act as defects on the substrate surface contributing to the formation of more blisters. At high concentrations, CNCs amplified an osmotic flow of water, favoring the blisters evolution and coalescence.

Another genre of nanocomposite was obtained through the addition of silver nanoparticles to MAPP-coated textile [88]. That strategy allowed not only a strong anchoring of those nanoparticles on a textile, but also tailoring its amount according to the duty cycle used during the deposition. A qualitative assessment showed the modified textile had antibacterial properties, acting as a reservoir of active biocidal species (Ag^+) (Figure 10).

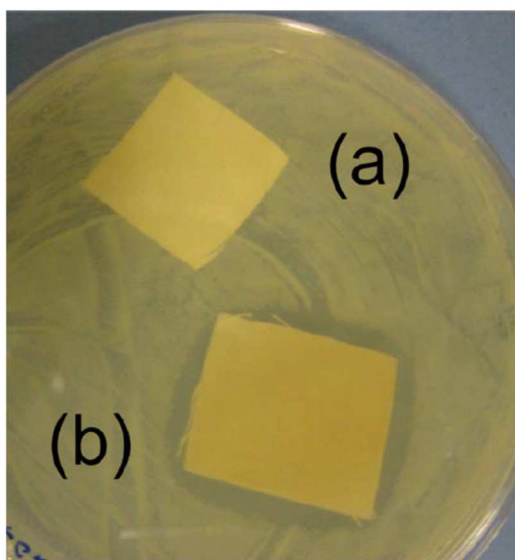


Figure 10 – Bacterial growth on agar plates in the surroundings of: (a) untreated textile and (b) textile covered with nanocomposite of MAPP and silver nanoparticles. Reprinted with permission from [88]. Copyright 2015 John Wiley and Sons.

In another study, silver nanoparticles were immobilized between MAPP layers; the outer layer acting as a controllable barrier for the flux of silver ions [89]. The properties of the substrate (PDMS) were exploited to control the barrier property of the outermost MAPP layer. Indeed, when it was stretched cracks were generated in the nanocomposite. They were perpendicular to the direction of the strain and were a consequence of the deposition of a stiffer polymeric layer (MAPP) over a flexible substrate (PDMS) [90]. The cracks affected the flux of Ag^+ and thus had an effect on the antibacterial properties of the surface. A similar

approach was used on poly(propylene) surgical mesh substrate [91]. Thanks to the open/close crack system, it was possible to adjust the flux of the antibacterial agent and to modulate the bacterial colonization on the biomaterial. The effect of ageing and sterilization procedures were further examined [92]. These nanocomposites are good examples of how the properties of plasma polymers can be combined with those of other materials in designing unique applications.

8. Multilayers

A great advantage of plasma-enhanced chemical vapor deposition process is the possibility of generating considerably chemically different coatings in the same reactor, through the change of the precursor used. That feature has been explored to promote the combination of different plasma polymers, to improve a specific property of the final coating. For instance, the adhesion of MAPP on gold substrates could be improved by the use of a silica-like plasma polymer interlayer deposited from a mixture of hexamethyldisiloxane and oxygen [93]. An optimum stability was obtained when the interlayer was treated with an oxygen plasma before the subsequent deposition of MAPP. The variation of the position of the sample inside the reactor and of the precursor during plasma polymerization allowed the development of textiles with Janus wetting properties [94]. In a “downstream” configuration, a fluorinated acrylic precursor was used to provide a coating with superhydrophobic properties to one side of the textile. In another configuration of the same reactor, maleic anhydride was used with the goal of providing superhydrophilic properties to the other side of the textile. Those results evidence the potential use of plasma polymerization to fabricate coatings with Janus properties (Figure 11).

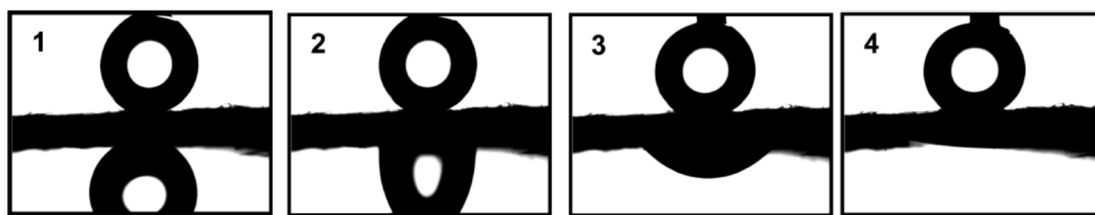


Figure 11 – Series of video frames illustrating the behavior of two water droplets simultaneously deposited on each side of treated textile. The top corresponds to the superhydrophobic side (only fluorinated precursor deposited) and the bottom the superhydrophilic side (first layer of fluorinated precursor deposition with subsequent deposition of MAPP). Reprinted with permission from [94]. Copyright 2016 American Chemical Society.

The possibility of generating corrosion resistant coatings, through hindering water penetration, is of interest for many industrial applications. Aiming that application Zhou et al. 2018 [95] have evaluated the water penetration and its effect on the corrosion of aluminum coated with plasma polymers of maleic anhydride (hydrophilic coating) or hexamethyldisiloxane (hydrophobic coating). The authors observed that the hydrophobic coating conformality was not changed upon exposition to water and that coating protected the aluminum from a salt solution up to a month. In contrast, MAPP failed in a day as the interfacial interaction and surface morphology were disrupted by the readily diffusion of water. Although water penetration might limit the direct use of MAPP as protective layers against corrosion, its adhesive properties were nicely explored for that application in a further study from the same work group [96]. In that study, the role of plasma polymers as a primer layer between aluminum substrates and a micrometer-thick polyurethane topcoat applied with a drawdown bar was analyzed. The use of a plasma polymer of hexamethyldisiloxane (HMDSO) between the polyurethane and the aluminum provided a better corrosion resistance, when compared to a control where only the polyurethane was deposited on the aluminum.

However, a relatively low pull-off adhesion between the two polymeric layers was observed. That last issue was addressed by the deposition of MAPP over the hydrophobic layer, or by changing the surface composition via nitrogen plasma (Figure 12).

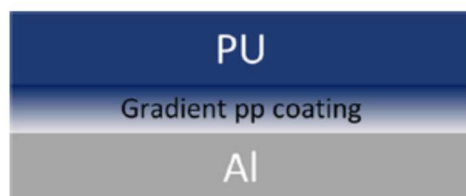


Figure 12 – Schematic representation of the multilayer system. Gradient pp coating represents a plasma polymer (pp) layer of HMDSO deposited over aluminum (Al) with either a subsequent deposition of MAPP or nitrogen plasma treatment. PU represents the polyurethane topcoat. Reprinted with permission from [96]. Copyright 2020 American Chemical Society.

9. Fabrication of Micro- and Nanostructured Surfaces

Due to their inherent micro- or nanoscale, plasma polymers are compelling to be used in precise and controlled development of structures through different nanofabrication procedures. In this section we aim to provide an overview that includes from relatively simple approaches to more complex ones and highlight some potential scientific and technical challenges that could be addressed for a greater integration of plasma polymers in micro-/nanopatterning.

The fact that plasma polymers are thin films that homogeneously deposit over a surface allows the transferring of topographical features of the substrates to the final film. For instance, plasma polymerization of maleic anhydride was performed on a substrate embossed with a copper grid [97]. After the removal of the grid, a grafting from procedure, through nitroxide-mediated radical polymerization, provided polystyrene polymer brushes in the areas

where MAPP was deposited. Another approach used copper grids as a photomask to UV irradiation [98]. Photooxidative etching of exposed regions was observed, which in turn affected the yield of a subsequent polystyrene grafting.

Soppera and co-workers [99, 100] described a simple and flexible method to prepare micro- and nanopatterned reactive surfaces by a combination of plasma polymerization and DUV interferometry using an excimer laser. The method involved the deposition of MAPP followed by aminolysis reaction of anhydride groups with propylamine and subsequent annealing at 120 °C (imidization). The DUV exposure of some plasma polymer areas modified the nature of the chemical species through surface ablation (Figure 13). Moreover, a large variety of morphologies could be obtained and their geometry could be easily adjusted by tuning the exposure condition.

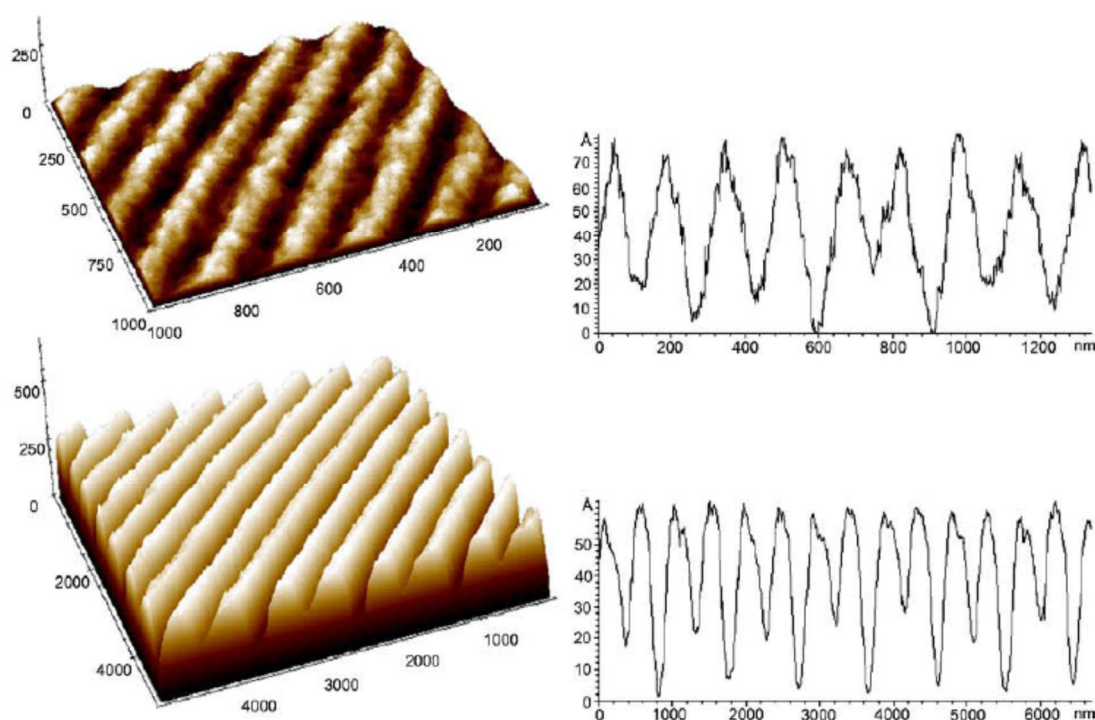


Figure 13 – Modification of MAPP by spatially controlled DUV irradiation. Reprinted with permission from [100]. Copyright 2009 Elsevier.

Careful investigations revealed that a higher sensitivity to DUV irradiation was reached for the imidized MAPP [100] deposited at low duty cycle (thus less crosslinked) [101]. Information concerning the precise tuning of the local surface chemistry was obtained through atomic force microscopy (AFM) in pulsed force mode, showing that the surface chemistry could be changed from hydrophilic to hydrophobic by changing the irradiation parameters [101]. Adhesion of eukaryotic cells and bacteria were tested on similarly patterned surfaces [102]. An opposite behavior of the cells and bacteria in terms of adhesion, proliferation and orientation on the nanopatterned surfaces was observed. Although it was not possible to decouple the role of the various factors involved in the study on the cell/bacteria behavior (chemistry and topography of the surface, adsorption of biomolecules, cell-type-specific response), the article presented the potential of this plasma polymerization-based process in the biomedical field.

In another study, the combination of immobilizing nucleophile-containing inks on MAPP and UV lithography resulted in the development of photo-rewritable surfaces [103]. One of the explored approaches used the aminolysis reaction of the dye with MAPP followed by exposure to UV light through a photomask. The lithography process patterned the surface by removing the dye molecules with it and leaving available carboxylic acids for further reaction. The latter could react with another dye to produce bifunctional patterned surfaces (Figure 14). Other photolithographic techniques have been tried out and showed the selective attachment of antibodies [104].

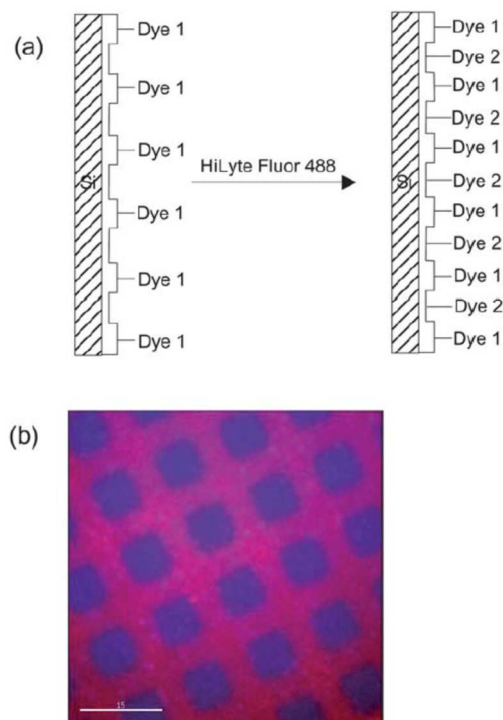


Figure 14 – Bifunctional patterned surface. (a) Scheme showing dye 2 (HiLyte Fluor 488) immobilization. (b) Fluorescence microscopy of patterned surface with dye 1 (cresyl violet perchlorate) and dye 2. Reproduced with permission from [103]. Copyright 2011 Royal Society of Chemistry.

Plasma polymerization offers the possibility of obtaining nanostructured surfaces in a single step, through the heterogeneous growth of the polymer on the substrate [105]. That feature has also been explored for MAPP thin films and it was shown to be affected by the substrate chemistry [106]. Brioude et al. [107] reported for the first time the possibility of controlling *ab initio* the microstructuration of MAPP thin films during a pulsed plasma process via adjustment of the deposition parameters. In the experimental conditions explored, three different structures were observed, namely beads, branches and needle-like structures. The morphogenesis of the structures comprised two steps: (1) the formation of activated species on the surface of the substrate by positive ions bombardment during the pulse on-time and (2) diffusion of the radicals over the substrate until it reached and reacted with the nearest

activated site. Thus, the formation of the structures require enough power to create the activated sites and their development is favored by short pulse on-time and long pulse off-time. Analysis of structures growth kinetics revealed the initial formation of the beads in the very early stage of deposition and proceeded with their random development into branched or needle-like structures (Figure 15) [108]. Although conventional chemical characterizations, such as FTIR and XPS, could not evidence chemical differences due to the presence of structures, analysis at the nanoscale via chemical force titration showed the existence two pK_a ascribed to the first and second deprotonation of dicarboxylic groups. Although, shifting in the pK_a values might indicate a different distribution of the functional groups on the surface, it might mainly be attributed to differences in the environment around the functional group.

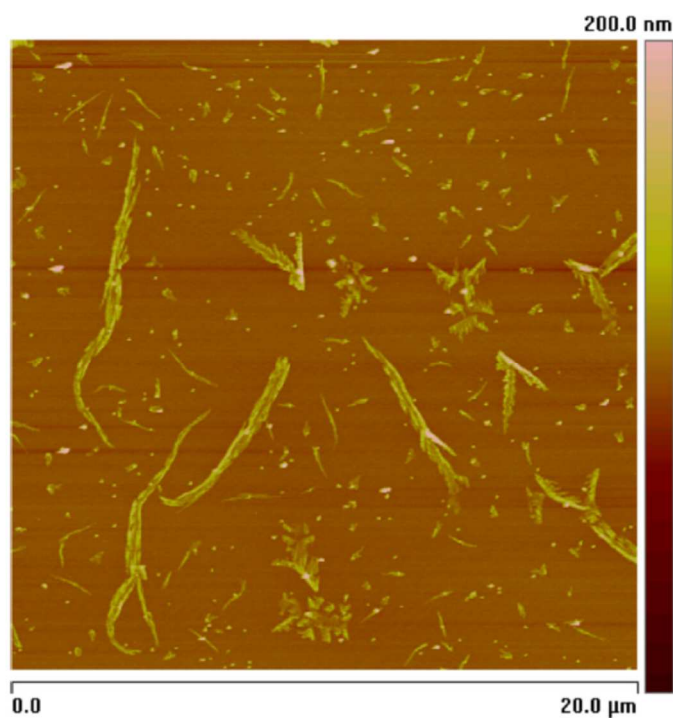


Figure 15 – AFM height image of MAPP evidencing the presence of micro- and/or nanostructures. Reproduced with permission from [108]. Copyright 2015 John Wiley and Sons.

The varied possibilities of nanostructuring of plasma polymers open up for the great range of applications that controlled surface topographies can promote. The *in situ* growth is of even bigger interest, as it can allow a one-step procedure of polymer structuration of a surface, once the conditions that control such growth are fully elucidated. That could bring even more innovation and versatility to plasma polymers and it constitutes an encouraging field to explore.

10. Conclusions

Plasma polymerization constitutes an interesting approach for bringing physico-chemical and morphological changes to a variety of substrates. In this review, the basic mechanisms of plasma polymerization and how they might impact the film properties were discussed using plasma polymers of maleic anhydride as examples. Plasma polymerization of maleic anhydride is advantageous when compared to other functionalization processes due to its straightforward approach to provide anhydride functional groups to a surface. However, a duality between higher amount of functional groups and its impact on crosslinking/stability of the thin films implies that a careful control and analysis of the polymer properties are demanded prior to any application. A discussion of how some physico-chemical properties of maleic anhydride plasma polymers affect its final properties was done. Furthermore, the potential of chemical derivatization to bring new functional groups, and consequently new applications, is one of the main explored routes. It shows a great potential to covalently or ionically attach desired molecules onto a surface or to increase adhesion among a surface and an object (another surface, molecule, cell, etc.). It is also possible to combine the substrate and plasma polymers properties for the generation of new materials, as mechano-responsive ones for example. Furthermore, the possibility of designing nanoscale structures on a

substrate seems to be a promising future for the technology, especially if the control of the plasma polymerization achieves a degree of allowing controlled *in situ* patterning. To finalize, the examples of materials design through the lens of maleic anhydride plasma polymers present some interesting strategies. Nevertheless, many other possibilities are available for other precursors and their co-polymerization. The potential use of bio-based precursors and the constant advancements of nanotechnology also indicates that plasma polymerization can reckon with the demands of materials of the future.

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