AN ALTERNATIVE METALLIZATION PROCESS OF ADVANCED POLYMERS: DEVELOPMENT AND APPLICATIONS

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Abstract

The production of adherent metal coatings on polymers, especially fluoropolymers, is still an open issue for many applications. Many pre-treatment and metallization processes have been proposed which are either time/money consuming or limited to few specific polymers. In order to propose a versatile and simple process to face this issue, this thesis work is focused on the combination of open-air atmospheric-pressure plasma treatment and electrochemical processes for the metallization of advanced polymers. Plasma treatment, in particular, was performed to graft nitrogen-bearing functionalities that are known to coordinate with ionic palladium species in the activation bath. After plasma and activation with palladium, electroless copper metallization was usually performed. Also silver deposition was considered for specific applications.

The manuscript is organized in four chapters: the first proposes a literature review regarding atmospheric plasma, electrochemical metallization and plasma treatment applied to electrochemical metallization of polymers. In the second chapter, the basic principles of the characterization techniques, used during this research activity, are described. In the third chapter the experimental procedures are defined and in the fourth chapter results are discussed. In particular, the discussion is organized according to the polymeric materials studied during experimentation. The same pattern is followed for each polymer, namely KETASPIRE® KT-820 PEEK, HALAR® 350LC ECTFE and SOLEF® 60512 (plaques) or 80000 (foams) PVDF. At first, parameters and characterization results of plasma treatment are discussed, afterwards outcomes of electrochemical metallization are described and finally the performances of the metallized polymer for the selected application are studied by means of specific tests.

Looking at the big picture, it is possible to say that atmospheric plasma treatment is a suitable process to pre-treat polymeric materials with different chemical structures, e.g. aromatics (PEEK) and fluorinated (ECTFE and PVDF), in order to promote electroless metallization. Plasma treatment,
especially if performed in the suitable conditions, was found to increase the surface tension of the polymeric substrates, mainly due to a marked increase of the its polar component. The process of hydrophobic recovery was studied and was found to be temperature dependent. A model was proposed that implied the building of master curves and the determination of the activation energy for the process of hydrophobic recovery. Chemical analysis of the surface revealed that plasma treatment leads to the grafting of nitrogenated and oxygenated functional groups; while morphological characterization pointed out that the surface roughness of the polymers is not affected by the preferred plasma conditions. It was found that plasma parameters need to be optimized depending on the chemical structure and on the form of the polymeric substrate, therefore allowing to obtain continuous and homogeneous copper deposits with good adhesion levels. Nucleation of copper was found to occur with no induction time on all the studied plasma-treated polymers.

Moving to the specific applications, metal-coated ECTFE was proposed as flexible concentrator mirror. Spectral reflectance studies, performed on simplified samples revealed that good reflection properties can be obtained. Moreover the deposition of silver layers allowed improving the performances with respect to copper coated ECTFE samples. Two different applications were considered for copper coated PEEK films, depending on their thickness. Thermal and mechanical properties of thin, 6 μm thick, films were determined to quantify the effect of copper layers on thermal conduction/dissipation and apparent elastic modulus. This information was needed to validate the applicability of these samples as oscillating diaphragms for micro-speakers. Results revealed that thermal conduction/dissipation is highly increased by metallization and the effect on the mechanical properties can be tailored to obtain a good compromise. Secondly the applicability of thicker copper coated PEEK stripes as switches for circuit breakers was studied. In this case electrical and thermal responses of polymer-metal switches were studied, revealing that, modulating sample geometry, it is possible to control the actuation current and the thermal deflection. Finally PVDF foams were successfully coated with a continuous copper layer that allowed avoiding HF generation, which was met during flame resistance tests on bare PVDF foamed samples. The flame resistance test is part of the set of characterizations that are required, for new materials, from the aerospace industry.
Chapter 1

Principles and Background

1.1 Electrochemical metallization

Electrochemical metallization is one of the most widespread metal deposition technologies for both conductive and insulating substrates. Metals can be deposited from aqueous solutions containing their salts only if there are sufficient electrons available, so to reduce the metallic ion in solution to the zero-valence state. In order to obtain a metallic deposit, this exchange of electrons must occur at the solution/substrate interface. A first classification of electrochemical metallization techniques can be performed depending on the source of electrons: if these are supplied by an externally applied voltage, e.g. by a galvanostat/potentiostat, the process is referred to as electrolytic deposition. On the other end, if electrons are not externally supplied, the process is known as electroless or chemical deposition [1]. In both of these families of electrochemical deposition a further classification can be performed, as shown in Figure 1.1. The electroless process includes immersion, contact and reduction (or autocatalytic) depositions, while electrolytic plating can be distinguished depending on the electrical signal, i.e. DC plating and AC/pulsed current plating.
1.1.1 Electroless deposition

Although electroless deposition includes three different processes, it is usually associated to reduction deposition. Immersion deposition, also known as galvanic displacement, is driven by the different reduction potential of the metallic substrate being dipped in the solution and the metal ions that are dissolved in this solution [2]. For example, when metallic zinc is immersed in a copper sulphate solution, an exchange of electrons occurs between metallic zinc and copper ions that leads to the dissolution of the first and to the deposition of the second. The reaction can be represented as:

\[
\begin{align*}
\text{Oxidation (anodic process):} & \quad \text{Zn}^0 \rightarrow \text{Zn}^{+2} + 2e^- \\
\text{Reduction (cathodic process):} & \quad \text{Cu}^{+2} + 2e^- \rightarrow \text{Cu}^0 \\
\text{Overall redox reaction:} & \quad \text{Zn}^0 + \text{Cu}^{+2} \rightarrow \text{Cu}^0 + \text{Zn}^{+2}
\end{align*}
\]

The redox reaction continues, ideally, until metallic zinc is exposed to copper sulphate solution, and stops once the whole surface is covered with copper. Therefore immersion plating can be adopted to produce thin layers of metal on metallic substrates having lower redox potential, and it stops once the solution can’t access the substrate. For this reason it is limited to applications where metallic substrates need to be covered with thin layers, usually of noble metals.

Reduction plating, more commonly addressed to as autocatalytic or electroless plating, has a broader application field than galvanic displacement for several reasons, including the possibility to deposit on insulating substrates and the direct proportionality between immersion time and deposit thickness. Commercial baths usually contain a dissolved metal salt, one or more complexing agents and stabilizers, a buffer, and a reducing agent. The first is the source of metal ions, complexing agents are needed to stabilize such metal ions in solution while the reducing agent is necessary to provide electrons to the system. Stabilizers are usually present in few ppm and can affect deposition rate, deposit morphology and bath decomposition rate. Deposition rates are determined mainly by diffusion of metal ions and reducing agent to the substrate surface. Moreover, since no external voltage is applied, the whole surface is at the same potential, i.e. the mixed potential of the system, and the deposition rate is the equal in every position of the object being plated. Examples of deposition reactions for some reducing agents are given in Table 1.1, it is to be noted that hydrogen is the principal by-product for every reaction mechanisms.
Table 1.1 Deposition reactions classified depending on the reducing agent [3].

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<th>Anodic reaction</th>
<th>Bath pH</th>
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<td>formaldehyde</td>
<td>$M^{x+} + xe^- \rightarrow M^0$</td>
<td>$2 \text{HCHO} + 4 \text{OH}^- \rightarrow 2 \text{HCOO}^- + 2 \text{H}_2\text{O} + \text{H}_2 + 2 e^-$</td>
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<td>$2 \text{H}_2\text{O} + 2e^- \rightarrow 2 \text{OH}^- + \text{H}_2$ M = Cu, Ag, Au</td>
<td>$\text{HCHO} + 3 \text{OH}^- \rightarrow \text{HCOO}^- + 2 \text{H}_2\text{O} + 2 e^-$</td>
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</tr>
<tr>
<td>sodium hypophosphite</td>
<td>$M^{x+} + xe^- \rightarrow M^0$</td>
<td>$2 \text{H}_2\text{PO}_2^- + 2 \text{OH}^- \rightarrow 2 \text{H}_2\text{PO}_3^- + \text{H}_2 + 2 e^-$</td>
<td>4–5 or 8–10</td>
</tr>
<tr>
<td></td>
<td>$2 \text{H}_2\text{O} + 2e^- \rightarrow 2 \text{OH}^- + \text{H}_2$ M = Cu, Ni, Co, alloy deposits</td>
<td>$\text{H}_2\text{PO}_2^- + 2 \text{OH}^- \rightarrow \text{H}_2\text{PO}_3^- + \text{H}_2\text{O} + 2 e^-$</td>
<td></td>
</tr>
<tr>
<td>sodium borohydrate</td>
<td>$M^{x+} + xe^- \rightarrow M^0$</td>
<td>$\text{BH}_4^- + 4 \text{OH}^- \rightarrow \text{BO}_2^- + 2 \text{H}_2\text{O} + 2\text{H}_2 + 4 e^-$</td>
<td>12–14</td>
</tr>
<tr>
<td></td>
<td>$\text{B(OH)}_4^- + 3 e^- \rightarrow \text{B}^0 + 4 \text{OH}^-$ M = Cu, Ni, Co, alloy deposits</td>
<td>$\text{BH}_4^- + 8 \text{OH}^- \rightarrow \text{BO}_2^- + 6 \text{H}_2\text{O} + 8 e^-$</td>
<td></td>
</tr>
<tr>
<td>aminoboranes</td>
<td>$M^{x+} + xe^- \rightarrow M^0$</td>
<td>$2 \text{R}_2\text{NHBH}_3 + 8 \text{OH}^- \rightarrow 2 \text{R}_2\text{NH} + 2 \text{BO}_2^- + 4 \text{H}_2\text{O} + 3 \text{H}_2 + 6 e^-$</td>
<td>5–10</td>
</tr>
<tr>
<td></td>
<td>$\text{B(OH)}_4^- + 3 e^- \rightarrow \text{B}^0 + 4 \text{OH}^-$ M = Cu, Ni, Co, alloy deposits</td>
<td>$\text{R}_2\text{NHBH}_3 + 7 \text{OH}^- \rightarrow \text{R}_2\text{NH} + \text{BO}_2^- + 5 \text{H}_2\text{O} + 6 e^-$</td>
<td></td>
</tr>
</tbody>
</table>

*aAfter hydrolysis of R₂NHBH₃.*
Differently from galvanic displacement, once a uniform deposit layer is formed on the substrate, the deposition process can proceed, since the deposit itself is catalytic with respect to the oxidation of the reducing agent and the simultaneous reduction of metal ions in solution [3]. Under this perspective silver baths are borderline, since its autocatalytic activity is so weak that only thin layers can be deposited unless the surface is repeatedly catalysed. Moreover, since oxidation of the reducing agent is the source of electrons, the number of metals that can be deposited using this process is limited to few the metal-reducing agent couples. Table 1.1 indeed, contains basically all the metals suitable for this process. Since many substrates are not catalytic, an activation step is usually necessary before electroless metallization. This can be based either on sequential immersion in an acidic stannous chloride solution followed by an acidic palladium chloride solution, or on a mixed palladium and stannous chloride solution followed by an acidic rinsing, to remove excess palladium before the deposition process. In either case, tin is necessary to reduce palladium ions to the metallic state, so that metallic palladium nuclei can act as a catalyst for the electroless system. A schematic representation of the deposition process is given in Figure 1.2. Metal-reducing agent couples are formed so that the metal reduction process is thermodynamically favoured. In order to increase kinetics, and therefore deposition rates, working temperature is usually higher than room temperature. For example, copper deposition baths using formaldehyde usually work between 40 and 60°C, while conventional hypophosphite-based Ni-P electrolytes work at higher temperature, from 80 to 90°C.

A specific case, which makes surface activation with a catalyst indispensable, is the metallization of insulating materials, including polymers. Plating on plastic (POP) was first performed in the first years of the 20th century, but its applications were limited until the early 1960s. The main reason for the previous lack of success was the poor adhesion between the polymer and the metallic deposit, which was solved by means of specific etching solutions and dedicated polymeric grades, e.g. ABS [4]. Before activation with the catalytic solution, the polymer surface must be indeed treated with an acidic etching solution and a neutralization bath. More information regarding this process will be given in the following.

Nowadays approximately 90% of the POP market is composed of ABS, ABS/PC blends and mineral-filled PA. This is mainly due to the lack of a suitable and versatile pre-treatment process that allows obtaining good adhesion levels between the polymeric substrate and the deposited metal layer.

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**Figure 1.2** Schematic representation of the electroless deposition process including redox reactions. At the moment of substrate immersion, left, and after the deposition process has started, right.
1.1.2 Electrolytic metallization

Unlike electroless metallization, which can be performed also on insulating substrates, electrolytic metallization requires the application of an electric field; therefore the substrate needs to be conductive.

When a metallic component is immersed in an electrolyte solution, a spontaneous dissolution may take place that involves the generation of metallic cations that migrate into the electrolyte. This phenomenon is called anodic dissolution and leads to the build-up of a positively charged portion of electrolyte close to the negatively charged metal surface [1]. Electrostatic charge attraction pulls the system to the opposite direction, i.e. positive metal ions back to the negative metallic surface, as a result a dynamic equilibrium condition is determined by the reaction:

\[ \text{Me}^0 \leftrightarrow \text{Me}^{x+} + x \text{e}^- \]  \hspace{1cm} (1.4)

Both anodic metal dissolution and cathodic deposition involve exchange of charges, therefore electric current flows in the system. By convention, the anodic dissolution current \( I_a \) is considered to be positive while cathodic deposition current \( I_c \) negative. At equilibrium the net current flow is nil therefore cathodic and anodic currents are equal in magnitude but opposite in sign, this equilibrium current is usually expressed per surface area and referred to as exchange current density \( i_0 \):

\[ |I_c| = |I_a| = i_0 \] \hspace{1cm} (1.5)

Electrolytic deposition, or electrodeposition, consist in a perturbation of such dynamic equilibrium in the cathodic direction so that the net current flow is different from zero and negative, causing the reduction of metal ions on the substrate. This is obtained through the negative polarization of the immersed metallic piece by means of an externally applied electric field. The difference between DC plating and AC or pulsed plating lies in the electric signal, while in the first case the applied voltage/current is constant, in the other two cases it can be either sinusoidal or a square wave. The key point is that to have metal deposition the average current flow in a period must be negative. Despite this difference, the basic components of an electrodeposition system are the same, namely:

- The electrolytic solution containing at least the metal salts
- Two electrodes immersed in the electrolyte, which work as anode and cathode
- An external power supply that is connected to the two electrodes

Similarly to electroless plating baths, the electrolytic solution usually contains: salts as sources of metal ions, buffers to control the pH, complexing agents to stabilize the metal ions in solution and several kinds of additives to control the deposition process as brighteners, grain refiners and levellers. The two electrodes are necessary to close the circuit, one is the metallic piece to be plated, usually called cathode or working electrode, while the other, usually called anode or counter electrode, serves to maintain the overall neutrality of the solution. Indeed if cations are consumed at the cathode, either anions must be consumed or cations generated at the anode. This dual option allows to classify anodes in two classes: sacrificial anodes and insoluble or inert anodes. In the first case the electrode is made of the same metal that has to be deposited, so that its dissolution releases metal ions to replace those that are reduced at the cathode. Insoluble anodes, typically consisting of platinum coated titanium, don’t supply metal ions but consume anionic species. It is to be noted that at the cathode also parasitic processes occur, as hydrogen evolution, which subtract electrons to the metal deposition process. A summary of cathodic and anodic process is given in Table 1.2.
Table 1.2 Redox processes at anode and cathode

<table>
<thead>
<tr>
<th>Cathodic processes</th>
<th>Anodic processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal deposition:</td>
<td>Sacrificial anode:</td>
</tr>
<tr>
<td>Me^{x+} + xe^{-} → Me^{0}</td>
<td>Me^{0} → Me^{x+} + xe^{-}</td>
</tr>
<tr>
<td>Parasitic H_{2} evolution:</td>
<td>Insoluble anode:</td>
</tr>
<tr>
<td>2H_{2}O + 2e^{-} → 2OH^{-} + H_{2}</td>
<td>2H_{2}O → O_{2} + 4H^{+} + 4e^{-}</td>
</tr>
<tr>
<td></td>
<td>4OH^{-} → 2H_{2}O + O_{2} + 4e^{-}</td>
</tr>
</tbody>
</table>

Finally, the external power supply is responsible for the polarization of the two electrodes in order to have accumulation of electrons at the cathode and depletion at the anode. Depending on the desired electric signal, it can be a DC, an AC or a pulsed power supply. A schematic representation for DC plating systems is given in Figure 1.3.

When performing electrodeposition it’s necessary to calculate the mass of metal being deposited, to determine the duration of electrolysis necessary to achieve a given thickness, to calculate the amount of reactants to be added in the electrolyte etc. In this perspective the Faraday’s law is very widely used in practice:

\[ m = \frac{QA}{nF} \]  \hspace{1cm} (1.6)

Where \( m \) is the mass of metal being deposited in grams, \( Q \) the charge passed through the circuit in coulombs, \( A \) the atomic weight of the metal, \( n \) the number of electrons necessary to deposit one atom of metal and \( F \) the faraday constant (\( F = 96485 \) C/mol). This equation can be applied to both ideal and real systems: in ideal systems \( n \) is equal to the valence of the metal reduction process (\( x \) of eq (1.4)), for real systems \( n \) also implicitly includes the efficiency of the process, this can be calculated by dividing the mass of metal being deposited in a given amount of time by the theoretical mass that should be deposited in the same time span [5].
1.2 Surface modification of polymers for wet metallization

Metallization of polymeric materials, resulting in a sufficiently strong bond between polymer and metal, is still a process where no universally accepted solutions have been proposed. Metal layers can be deposited on top of polymers mainly by dry (physical or chemical vapour deposition) or wet (mainly electroless deposition) processes [6–8]: in principle, dry processes allow to deposit a wide number of metals on several polymeric substrates, but adhesion levels are in most of the cases very low. Wet processes can attain higher levels of adhesion but the available spectrum of metals and, especially, polymers is narrow. Independently on the metal deposition process, surface preparation was found and accepted to be fundamental to obtain adherent polymer-metal interfaces. Since the last decades of the twentieth century, several technological solutions have been proposed to modify polymer surfaces, which span from wet chemical etching to dry chemical functionalization [7,9–11]. Independently on the modification process, several studies have been performed to understand the chemical-physical principles governing the adhesion mechanisms between polymeric and metallic materials: several theories have been proposed, including chemical bonding, mechanical interlocking, wetting theory and electrostatic theory [12]. In real cases, it is anyway complex to understand the actual contribution of the single mechanism on the final adhesion, even if it appears that particular combinations of polymers and processing favour one or more of these various forces [1,13,14].

The aim of this chapter is to give an overview of traditional and alternative surface preparation methods of polymers, focusing on the ones specifically developed for wet metallization.

1.2.1 Wet chemical etching

Wet etching is one of the three main steps involved in the electrochemical metallization of polymeric surfaces, the other two are surface activation with catalysts and electroless deposition itself [15]. The effect of wet chemical etching is dual: on one side polymer surface energy, and therefore wettability, are enhanced due the oxidative action exerted by chemicals in the bath; on the other end, surface roughness is highly increased to improve catalyst seeding and mechanical interlocking of the growing metal layer. This is translated in a substantial modification of the polymer surface that, due to the presence of holes and cavities and to the reactive group formation, is highly receptive to the catalyst and is both chemically and mechanically bonded to the metallic coating [16–18].

The effect of wet etching though is dependent on the polymer structure, therefore Plating on Plastic (POP) after this pre-treatment is limited to a small group of resins that includes ABS, ABS/PC blends and PA. These three represent more than 90% of the volume of polymers that are industrially metallized. The success of ABS and its blends is mainly due to the fact that it demonstrated adhesion levels of metallic coatings when subjected to wet etching, with chromic/sulphuric acid mixtures, which were about one order of magnitude higher with respect to those obtained on other polymers after mechanical roughening of their surface [15]. Several theories were proposed in the late ‘60s to justify the high adhesion values measured on ABS after wet etching, which included the presence of chemical forces binding polymer and metal: both Van der Waals interactions and valence bonds were thought to be present at the interface. More recently also Kisin [19,20] proposed that the surface composition of the polymer can play a role in the adhesion of the metallic coating. Specifically adhesion of copper coatings, obtained by sputtering and subsequent galvanic strengthening, on pristine ABS parts was found to increase in time together with an increase in the concentration of hydroxyl and carbonyl functionalities. In this case the authors can't determine whether surface oxidation is attributed to the metal deposition processes or to the oxidative action exerted by copper, but chemical interaction is thought to be fundamental for adhesion. The fundamental advantage of ABS with respect to other
resins is to be found in its structure, namely in the presence of butadiene spheroids that are dispersed in the acrylonitrile-styrene matrix [21]. During the treatment with chromic/sulphuric acid, butadiene is etched at a higher rate with respect to the matrix, therefore this allows the formation of superficial and sub-superficial voids and cavities that exert a dual action in the galvanic metallization process (Figure 1.4): during the activation step, they favour and increase homogeneous palladium seeding [22]. Once the galvanic deposition is performed, the adhesion is increased due to the presence of the so called mechanical interlocking between the rough polymeric surface and the metal.

![Figure 1.4 Schematic cross-sectional representation of: a, pristine ABS; b, ABS after chemical etching; c, ABS after activation with Sn-Pd colloidal solution; d, ABS after electroless metallization.](image)

Due to the high environmental and health concerns related to the utilization of hexavalent chromium [23,24], some alternative surface preparation processes have been proposed that make use of different etching agents. Cr(VI)-free surface conditioning was performed with solutions based on sulphuric acid with hydrogen peroxide and/or nitric acid without satisfactory results [25]. Wang and co-workers proved that H2SO4–MnO2 colloids can be adopted to replace, with similar results, CrO3–H2SO4 for the etching process of ABS. In particular it was demonstrated that this mixture allows reaching adhesion levels, of electroless copper, that are about 85% of the value obtained with chromic mixture [26]. Moreover, when this alternative etching mixture is ultrasound-assisted, adhesion is further improved to more than 95% the value obtained with chromic mixture [27]. Also in this case the morphological modification, leading to the formation of cavities, is associated to surface oxidation. The higher adhesion obtained with the ultrasound-assisted process is indeed justified by the increased concentration of polar carbonyl and hydroxyl groups. The authors also observe that adhesion level as a function of etching time shows a maximum and then decreases, this is suggested to be due to the dual nature of adhesion: chemical interactions increase with time as surface oxidation increases, while mechanical interlocking is maximum when butadiene spheroids are dissolved but the acrylonitrile-styrene matrix is still mechanically resistant [12].

Polyamide, due to its advantageous mechanical, thermal and frictional properties, is gaining much attention also in the plating industry, thus eroding part of the market that was previously dominated by ABS. Chromic acid also etches PA, but doesn't produce satisfactory results as for ABS; for this reason new processes have been specifically defined for this class of materials. Chromic mixture has been replaced by a two-steps process that relies on swelling and conditioning of the polymeric surface: swelling is performed by means of a solution with organic components and etching substances to assure homogeneous removal of inorganic fillers; conditioning is necessary to avoid dragging of the
components of the swelling solution in the activation bath [28–30]. Alternative processes also involve two steps: etching of the surface with acidic solutions containing fluoride and neutralization with alkaline bath prior to electroless metallization [31].

### 1.2.2 Alternative surface modification processes

The interest in replacing traditional etching solutions, containing Cr(VI), is confirmed by the presence of several works that propose alternative processes to prepare polymer surface to metallization, making also use of dry techniques and with particular focus on ABS. The attention to this material is justified by its huge market share, while the utilization of dry techniques is to be intended as an effort to reduce as much as possible the environmental impact of the process.

Water-based grafting of poly (acrylic acid) PAA has been proposed to allow wet metallization of ABS without the utilization of Cr (VI) etching solution and Pd (II) activation, as shown in Figure 1.5. Covalent surface modification of the substrate, independently on its nature, can be obtained by the so-called diazonium-induced anchoring process. This process is induced by redox activation of aryl diazonium salts in the presence of vinyl monomers: aryl diazonium salts are reduced with iron powder to produce radicals which, on one side, form a grafted polyphenylene-like film on the substrate surface and, on the other, allow initiation of the radical polymerization of the vinlyc monomer in solution. These radical-terminated macromolecules subsequently react with the polyphenylene primer layer to form an organic film on the surface. The resulting coating is highly adherent to the surface, therefore this process can be exploited as tie layer between the substrate and a metallic deposit [32]. When acrylic acid is added as vinlyc monomer, PAA films can be formed on the surface. At the suitable pH, carboxylate groups can act as complexing sites to immobilize Cu^{2+} ions, which can be reduced to metallic copper and act as catalyst for the electroless process. The advantages of this process are the substitution of chromic acid and the elimination of expensive palladium salts for the activation step[33]. At the same time the results, in terms of adhesion of the metallic layer, are dependent on the polymeric substrate: this is due to the fact that PAA is more easily grafted on polymer substrates that are more hydrophilic [22].

![Figure 1.5](image.png)

**Figure 1.5** Surface preparation of ABS substrates for electroless metallization by (a) the conventional industrial process and (b) the Cr- and Pd-free process
A comparison of several pre-treatments was performed by De Bruyn [34] on ABS, PP and PC and compared to the traditional chromic acid etching. Flame treatment, mechanical treatments (sandblasting and grinding), lacquer treatment, and oxygen plasma treatment were considered but results didn’t indicate a valid alternative to chemical etching.

Finally three different techniques were proposed by L. Magallón Cacho for surface modification of ABS, namely the optophysic treatment, the photocatalytic treatment and the optothermal treatment. The first is based on the alternation of corona treatment ad UV irradiation, the second involves the utilization of TiO₂ nanoparticles in suspension on the polymer surface under UV exposure and the last allows performing selective modification of the polymer surface using thermal laser ablation [35]. The optophysic treatment allows performing electroless deposition of metallic coatings on ABS due to specific surface modification mechanisms: UV treatment is believed to affect the sub-surface layers of the sample by creating oxidation by ozonolysis and traps charges due to PB reticulation, while corona highly oxidizes the outer layers. The combination of the two treatments moreover, causes the trapped charges to be released during corona; this release of energy and charges is converted into thermal agitation that causes dielectric and mechanical breakdowns, thus etching the cross-linked PB spheroids [36]. The photocatalytic treatment makes use of a suspension of TiO₂ nanoparticles in suspension under UV irradiation, preceded by corona exposure. Titanium dioxide under irradiation favours the formation of hydroxyl and superoxide radicals that are highly reactive and interact with the polymeric substrate, leading to micro-pore formation and oxidation. Results indicate that good dispersion of the catalytic nanoparticles, in contact with the substrate, is needed to obtain homogeneous surface modification [37]. In the optothermal treatment, ABS surface is at first sensibilized with Pd or Ag nanoparticles and therefore exposed to concentrated laser sources. Of course, in order to obtain suitable sensitization optophysic or photocatalytic treatments need to be previously performed. Low power laser exposure subsequently allows performing patterned metallic deposits on the polymer surface. The presence of metallic nanoparticles enhances thermal response to the optical stimulus, making the process more effective and rapid. The portions of the surface that are exposed are ablated with good efficiency, electroless metallization won’t therefore occur where the substrate has undergone the laser exposure [35].

Although promising, most of the alternative pre-activation processes described so far are limited to ABS, its blends with PC and few more materials. Therefore, since the aim of this work is to determine a versatile process to modify the surface and metallize a wide spectrum of polymers (including high performance aromatic and fluorinated thermoplastics), attention will be devoted in the following to plasma treatment, which was demonstrated to be promising on many polymeric materials.

### 1.3 Low and ambient pressure plasma discharges

Since the early ‘90s plasma technology has attracted much interest in the field of metallization of polymeric materials, mainly as pre-treatment to promote adhesion between the organic substrate and the metallic coating. Plasma was generally adopted to modify the surface of several classes of materials. Applications include dry cleaning, dry etching, surface functionalization, plasma assisted polymerization and adhesion promotion in numerous fields. If in its early times plasma was limited to low pressures, in recent years technological evolution allowed developing open-air and ambient-pressure plasma sources, this in turn opened new markets and new possibilities to this technology due to its competitive operational cost and higher flexibility.

Before giving an overview of the application of low and ambient pressure plasma processes to the metallization of polymers, a brief insight is proposed on plasma principles and technology.
1.3.1 Principles and technology of plasma

Plasma can be considered as a portion of matter that is neutral but composed by free charged particles moving in random directions. It is frequently defined as the fourth state of matter since it can be obtained by thermal excitation of a gas: at a sufficiently high temperature, molecules in the gas decompose to form a gas of atoms moving in random direction, if temperature is further increased a portion of atoms is decomposed into freely moving ions and electrons, this last is the plasma state. Additionally to thermal excitation of the gas, the plasma state can be obtained also due to the action of electric or electromagnetic fields. Most of the industrial applications of plasma make use of electrical energy: the electric field transmits energy to the electrons (the most mobile charged particles of the system) inside the gas, neutral species are therefore excited by collisions with the high energy electrons. Collisions can be elastic or inelastic, in the first case the kinetic energy of neutral species is altered, in the second the electronic structure of neutral species is modified with the creation of excited species or ions.

In thermodynamic equilibrium the density of electrons ($n_e$) is equal to the density of ions ($n_i$) and the same is valid for their temperatures, i.e. $n_e = n_i$ and $T_e = T_i$. The temperature required to form plasmas from pure substances in thermodynamic equilibrium ranges from 4000 K to about 20,000 K. Not all the particles inside plasma are ionized, therefore the fractional ionization ($x_{iz}$) of plasma can be defined as:

$$x_{iz} = \frac{n_i}{n_g + n_i}$$

where $n_g$ is the neutral gas density (cm$^{-3}$). Fractional ionization is higher if the portion of ionized species in the plasma is higher. It’s therefore possible to distinguish plasmas both depending on their fractional ionization and on the degree of thermal equilibrium. Usually plasmas in thermodynamic equilibrium are characterized by high gas and electron temperatures, while fractional ionization may range from a high percentage to less than 1 part per billion; these are frequently defined as hot or thermal plasmas. On the contrary, cold plasmas are not in thermodynamic equilibrium and therefore electron temperature is much higher than heavy particles temperature, this is due to the fact that mobile electrons are more easily heated than relatively high mass ions or neutral particles. Figure 1.6 reports a graphical representation of different plasmas, where classification is performed depending on charge density and electron temperature.
It's possible to notice that industrial plasmas are characterized by a broad range of electron temperature and charge density. Taking into account low-pressure glow discharges, electron temperature is usually much lower than ion temperature; for this reason generation of radicals, etchant atoms, ions, and deposition precursors from the feedstock gas is due to collisions with energetic electrons. Electron temperature is usually lower than the threshold value for ionization ($E_{iz}$) and dissociation ($E_{dis}$) of the feedstock gas, therefore the distribution of $T_e$ plays a crucial role: defining $g_e(E)$ as the number of electrons per unit volume with energy $E$, then a qualitative representation of the distribution function can be given as in Figure 1.7. Only the high-energy tail of the Maxwellian distribution produces ionization and dissociation of the feedstock gas molecules, while electrons with energy lower than $E_{iz}$ and $E_{dis}$ cannot generate charged particles.
A broad range of plasma sources is used in industry, examples include but are not limited to [39,40]:

- **Thermal plasmas**: Its application for remelting of metals in arc furnaces and for welding is well known. Plasma spray has been applied with success for surface coating, initially in the aerospace industry. Today, application of plasma spray technology is widespread in several industrial fields, including the automotive industry, the medical implant industry, the oil & gas industry and the cutting tool industry.

- **Low pressure plasma** is used in many crucial steps of integrated circuit production, dry etching and surface modification are just some examples.

- **Plasma enhanced chemical vapour deposition (PECVD)** is also used to deposit thin films for applications in several fields. One advantage with respect to conventional CVD is the lower deposition temperature.

- **Atmospheric pressure dielectric barrier discharge (DBD)** is widely employed to increase wettability of polymeric films for further processing as printing or lamination [41].

Success and variety of application of plasma technology are a result of the multiplicity of parameters and conditions that can be accessed and adopted: highly reactive species can be generated at low gas temperatures, thus allowing performing surface modification on temperature-sensitive materials. The substrates may be in direct contact with the plasma, biased relative to the plasma, or placed downstream from the plasma.

Since industrial applications make use of both low-pressure and ambient-pressure discharges, in the following a brief overview will be given on both plasma sources. Surface modification of polymers though is industrially performed mainly through atmospheric pressure technology, due to higher versatility and lower costs with respect to low pressure processes. Moreover mainly cold plasmas will be considered, i.e. plasmas that are not in thermodynamic equilibrium, due to the lower gas temperature that is necessary to treat polymeric materials.

### 1.3.1.1 Low pressure plasma sources

Low-pressure plasma sources are historically the first to be commercially available. Due to the lower pressure inside the plasma chamber, it is indeed easier to obtain a stable glow discharge at lower power with respect to atmospheric pressure systems. Nowadays low-pressure plasma sources are mainly employed in the semiconductor industry for fundamental steps of the integrated circuit production as etching and sputtering [42]. It is possible to distinguish plasma sources depending on
the mechanism of gas excitation [43]; it is therefore suitable to divide such sources among direct current, radio frequency and magnetron plasmas.

The DC source is the simplest; two electrodes, an anode and a cathode compose it, in a vacuum system, Figure 1.8. The discharge is generated if the adequate voltage is applied between electrodes at the appropriate gas pressure. Ions are accelerated to the negative electrode, due to the presence of a strong electric field in its proximity, and cause the generation of secondary electrons. These are accelerated back to the opposite electrode gaining significant energy; this energy is transferred to neutral species therefore generating more ions to sustain the discharge. Due to the poor energy transfer efficiency of secondary electrons, leading to a low fractional ionization of the plasma phase, this technological solution has nowadays been replaced by more advanced systems. Moreover, diode plasmas cannot be operated if the cathode is insulating, it may occur also if oxides are formed on the surface due to the presence of oxygen in the chamber.

Radio frequency discharge chamber is similar to the DC diode chamber, the only difference is the oscillation of the electric field at high frequency, most commonly at 13.56MHz. The oscillation of the electric field has some advantages: insulating surfaces can be treated/deposited due to elimination of charge build-up and electron motion is enhanced. This last effect is particularly important since it increases the probability of inelastic collision and therefore of ionization by means of secondary electrons. The direct consequences are increased ion currents and faster sputtering processes. To maximize the power transfer, an impedance matching network is required, this is usually placed in a “matchbox” near the vacuum chamber. The most common example is the “L network”, which is composed by two capacitors and an inductor.

Microwave plasmas are generated by means of magnetrons; the usual excitation frequency is 2.45GHz, which implies that only light electrons are directly excited by the electromagnetic radiation. Due to this fact the fractional ionization of the plasma is higher with respect to RF and DC sources [44]. Several reactor geometries are available for this class of plasma sources. The classification performed by Marec and Leprince [45] identifies three different configurations: closed structures, open structures and resonance cavities. One of the most used configurations is the waveguide coupled reactor: in this configuration, microwave radiation is transported by means of rectangular waveguides into a resonator that surrounds a dielectric tube, which represents the actual plasma chamber. Many other configurations exist but are not reported here [44,46,47].
1.3.1.2 Cold atmospheric pressure plasma sources

Atmospheric plasma sources can be distinguished depending on their excitation mode, namely DC and low frequency discharges, radio frequency discharges and microwave discharges. Increasing the excitation frequency affects the behaviour of electrons and ions: given their lower mass, only electrons can follow the oscillations of the electric field in the radio and microwave frequencies, while ions are characterized by lower oscillation frequency [48]. Among low frequency and DC discharges another distinction needs to be performed between current carrying arcs and transferred arcs (Figure 1.9). In the first case the nozzle is positively charged and acts as anode, the plasma atmosphere is therefore ejected towards the substrate due to the gas flow. In the second case the substrate is the anode, and therefore the discharge is spontaneously formed between the cathode and the work piece. DC plasma torches based on transferred arcs are usually characterized by high thermal load and are therefore used for cutting, melting and welding [49].

![Figure 1.9 Schematic cross sectional view of current carrying (left) and transferred arc (right)](image)

Pencil-like torches are relevant since, differently from transferred arc torches, are based on low power, current carrying arc plasma jet. This allows generating small amounts of heat, thus permitting to treat temperature-sensitive materials with chemically reactive plasmas. Many commercial products are therefore available to prepare a wide range of surfaces, prior to joining with adhesives, coating or printing. This technological solution is preferentially adopted when complex surfaces need to be treated, due to its versatility: reduced dimensions and weight allow movement of the plasma source using multi-axes robots. Examples of application include the automotive and packaging industries. Also bi-dimensional substrates can be treated (textile industry), in this case arrays of plasma torches are needed to avoid excessive operational time.

Another example of cold plasma is the corona discharge; this is based on pulsed DC excitation between a cathode wire and an anode (usually the object to be treated). Pulse duration is tailored so that it’s shorter than the time necessary for arc creation, so that plasma produces a glow around the cathode tip but no arcs are formed [48]. Due to the limited plasma volume, related to the small dimension of the cathode wire, only small surfaces can be treated, to overcome this problem the setup can be modified adopting a planar electrode parallel to the surface to be treated. This system is affected by the generation of micro-arcs that always initiate in the same position leading to non-homogeneous treatments of the material surface. For this reason dielectric barrier discharge plasma (DBD) was developed, Figure 1.10. This device consists of two parallel electrodes (in the simpler configuration they are planar), where at least one is coated with a dielectric layer. This insulating layer is added in
order to limit the discharge current, thus avoiding the arc transition, and to randomly distribute streamers on the electrode surface ensuring a homogeneous treatment. The gap between electrodes is usually limited to few millimetres and the plasma gas is flown through it. The excitation source can be both pulsed and sinusoidal. The discharge regime depends on the precursor gas, e.g. He is known to favour glow discharge rather than filamentary ones. The geometry of DBD equipment can be modified to treat different geometries, but the majority of instruments are designed to treat bi-dimensional surfaces, i.e. films and fabrics.

Among cold radio frequency (RF) discharges the atmospheric pressure plasma jet is the most relevant and widespread (Figure 1.11). This system usually consists of two concentric cylindrical electrodes through which the gas is fed, the inner electrode is polarized and the outer is grounded; the plasma species are generated between the electrodes and expelled due to the high gas flow, similarly to pencil-like torches. The applied voltage is usually between 100 and 150 V and the gap in the order of few millimetres, this allows producing a stable discharge avoiding arc transition.

Figure 1.10 Schematic representation of cathode wire corona discharge (left) and DBD (right).

Figure 1.11 Schematic representation of a RF plasma jet (left) and a microwave induced plasma torch (right).
The working principle of microwave induced plasmas (MIPs) is roughly the same for all systems [50]: a power source generates the waves, these are guided along the system by specific guides and finally excite the gas electrons. Due to the high frequency of excitation, heavy particles remain static and electrons are accelerated, thanks to inelastic collisions between electrons and heavy particles finally neutral species are ionized and dissociated to form the plasma. Once started, the discharge is stable but ignition can be an issue, for this reason several methods are suggested to concentrate microwave energy: examples include resonant cavities that allow signal amplification and utilization of a conductive rod that acts as antenna concentrating microwaves at its tip. The main classes of atmospheric pressure MIPs are resonant cavity plasmas and free expanding torches. Resonant structures are designed so that a specific wavelength is able to travel in the cavity generating a standing wave, the resonance frequency depending on the geometry of the cavity. It’s therefore fundamental to tailor geometrical parameters with respect to the adopted wavelength. Metallic free expanding torches make use of the wave guide-to-coaxial line transition, i.e. microwaves are generated by the magnetron source and reach the working gas using rectangular and coaxial guides. The working gas is flown through an inner coaxial line conductor and is ignited on top of the nozzle. Slightly different structures are necessary if the plasma gas flows inside an insulating material.

1.4 Plasma modification and wet metallization of polymers

Starting from the last decade of the 20th century interest was devoted to the application of plasma technology to the metallization of polymeric materials. The chemical modification, induced by suitable plasma treatments, is known to improve adhesion of several types of coatings to polymeric materials [10]. Improved bonding is due to several factors including higher surface energy and, in some cases, specific chemical interactions between the plasma-modified surface and the coating. In the following a chronological overview of plasma modification for electrochemical metallization of polymers is given.

One of the first examples, present in the literature, regarding the utilization of plasma modification to increase adhesion of a metallic layer to a polymer isn’t actually associated to electrochemical deposition techniques. In that case [51], PP was treated at two different frequencies, 70kHz and 13.56MHz, in two plasma atmospheres, namely NH3 and N2, at low pressure. After surface modification Al was deposited by thermal evaporation. It was demonstrated that NH3 based plasma is more effective than nitrogen plasma in terms of nitrogen incorporation; this is reflected both in the surface energy of the treated surface and in the adhesion levels of the Al coating. Finally the work of adhesion was calculated from contact angle measurements, showing a distinct dependence on the pH value of the different solution adopted. This led to suggest that acid-base interactions are present at the surface.

The firsts to propose plasma as a pre-treatment prior to electroless metallization of polymers were Charbonier, Alami and Romand [52]. PC and PS were subjected to different pre-treatments, namely conventional chemical etching and O2, NH3 and N2 plasmas. Two different activation solutions were adopted prior to immersion in the electroless nickel bath: in one case SnCl2-based followed by PdCl2-based solutions and in the other a mixed PdCl2/SnCl2 solution. Different Pd chemisorption mechanisms were proposed depending on the pre-treatment and on the activation processes: nitrogen-containing functional groups on the surface are believed to favour Pd adsorption limiting that of Sn, on the contrary oxygen-containing functionalities favour Sn adsorption. When oxygen is grafted on the surface Sn is directly coordinated, while Pd is coordinated to Sn by Cl; when nitrogen is present nitrogen is directly interacting with the surface (Figure 1.12). This was verified by XPS analysis, comparing the results from the different pre-treatments and activation processes.
The same behavior was observed in another study, performed on PS and PI [53]. In this case, differently from the abovementioned, SnCl₂-based followed by PdCl₂-based activation was compared to PdCl₂-based activation. The authors confirm the interaction model proposed between the plasma treated surface and the activation solution with a further hypothesis: nitrogen-containing surfaces not only interact directly with palladium ions but the presence of nitrogenated groups hinders tin chemisorption even if oxygen functionalities are present. On the other end, surfaces functionalized solely with oxygen will not interact directly with palladium ions, therefore their chemisorption can occur only after immersion in the SnCl₂-based solution. Tin indeed, directly chemisorbs on oxygen-only functionalized surfaces. Moreover, it was demonstrated that surface pre-treatment with plasma can be adapted to functionalize different classes of polymeric materials, as shown in Table 1.3. This is of paramount importance since it confirms that, in principle, it’s possible to functionalize different polymers with the same equipment.

The same authors also studied the initiation time of electroless deposition depending on the activation process [54]. Apart from considerations regarding the catalytic action of palladium depending on its oxidation state, the authors confirm that direct Pd chemisorption occurs on plasma treated surfaces containing nitrogenated groups. Therefore one-step activation with PdCl₂ is feasible. At the same time, the high surface concentration of Pd, measured by XPS, probably results from both chemisorption and physisorption. This implies that not all the Pd²⁺ ions are strongly bound to the polymer; therefore a competitive process takes place during the initiation stage involving both reduction of Pd²⁺ to Pd⁰ and dissolution of the weakly bonded Pd²⁺ ions, resulting in a reduction of the catalyst surface concentration that is higher the longer the initiation time.
Once atmospheric pressure discharges began to spread in the scientific community, the first attempts were performed to apply this new form of plasma technology to the galvanic metallization of polymers. Comparative studies have been performed regarding the effect of direct plasma treatment and UV irradiation on the electrochemical metallization of polybutyleneterephthalate and other polymers [55]. A DBD equipment was used in air or in reactive mixtures at ambient pressure, the discharges were generated at 10kV and frequencies ranging from 15 to 150kHz. The effect of plasma was compared to nearly monochromatic UV irradiation at different wavelengths; results indicate that: ABS surface after plasma results in a similar morphology to that obtained after chemical etching but owning higher wettability, while mineral-filled PA shows selective etching of the polymeric matrix. On the other end no morphological alterations were obtained after UV irradiation. Surface energy was increased after both pre-treatments, with higher values for short wavelength UV sources. This is reflected in the metallization of PBT: adhesion of metallic deposits, obtained with commercial solutions, was increased from 0.13 N/mm² for the untreated polymer to 6-8 N/mm² for the UV irradiated surface. Also plasma treated surfaces demonstrated improved adhesion with respect to the pristine substrate, but lower performances were achieved with respect to the UV pre-treatment.

With the increased interest in the utilization of plasma as alternative adhesion improvement process, many research groups started to focus on the understanding of the chemical and physical modification induced by plasma treatment on polymers in order to determine their interactions with coatings, including metals [7]. The group of Charbonier, Alami and Romand continued demonstrating the possibility of performing electroless metallization with simplified activation procedures thanks to the introduction of nitrogenated groups by plasma [56]. In this case the authors demonstrate that Ni-P and Cu can be deposited by electroless on PC samples treated in a RF plasma reactor at low pressure. Moreover Pd²⁺ ions, chemisorbed in the activation step, can be reduced by the hypophosphite ions (H₂PO₂⁻) present in the Ni-P deposition bath but cannot be reduced by formaldehyde (the standard reducing agent for electroless copper solutions) unless Sn²⁺ ions are present. In successive studies, the authors confirm what previously mentioned and claim that electroless deposition can occur only after a sufficient portion of the chemisorbed Pd²⁺ is converted to metallic palladium [57,58].

The study of nitrogen and oxygen functionalization by means of plasma sources continued attracting attention on several polymeric materials, both aromatic and fluorinated [59,60], and some reaction mechanisms have been proposed depending on the chemical structure of the polymer. Also the nature of the excited species present in the plasma atmosphere has been considered [61]. In particular, adhesion of evaporated metallic coatings was determined depending on the plasma gas utilized in a low pressure RF reactor. It is demonstrated that N₂/H₂ mixtures can be used in place of ammonia with satisfactory results in terms of metal adhesion and higher environmental sustainability. The nature of metastable charged species, generated in ammonia and N₂/H₂ mixtures, is believed to be the key for the functionalization of the polymeric surface, resulting in higher adhesion of the metallic coating.

Once the advantages of atmospheric pressure plasma pre-treatment of polymers for subsequent electroless metallization had been demonstrated, its application to complex surfaces started to be proposed. An example is the electroless plating of nonwoven polyester fabrics after atmospheric pressure plasma treatment [62]. In this case pure nitrogen gas was fed in the process chamber, therefore plasma discharge occurs at atmospheric pressure but not in open air, Figure 1.13. This allows having a better control of the discharge, avoiding the presence of contaminants as oxygen, without the need of expensive low pressure equipment.
Results indicate that short plasma exposure times, about 1s, are sufficient to graft nitrogen-containing functionalities on PET surface, thus allowing the production of uniform and adherent deposits of Ni-P by electroless deposition.

Besides surface functionalization with simple gases, e.g. air, oxygen, nitrogen or noble gases, also surface deposition of thin layers can be performed with plasma. Originally this process was limited to low pressure systems, PECVD is a clear example, but in time also atmospheric pressure systems have been adapted for this purpose. Studies have been performed at the Fraunhofer Institute that combine three elements: patterned plasma treatment, deposition of silanes and electroless metallization [63]. The patterned surface modification, obtained using an appropriate experimental set-up Figure 1.14, is usually referred to as plasma printing. He and aminopropyl-trimethoxysilane (APTMS) have been used as carrier and precursor gas respectively, yielding films 20 to 50 nm thick containing primary amino groups. Successive metallization was performed, after activation with a PdCl₂ based solution, with both electroless copper and Ni-P baths. Results demonstrate that the process is reliable at the sub-millimetre scale and that the factor limiting resolution is the accuracy in the production of the masks for the patterned plasma treatment.
Joined studies were also performed by French and Romanian research groups on the plasma treatment of PVDF for subsequent electroless metallization [64–66]. In these cases low pressure equipment was adopted and a comparison was performed between RF and microwave plasmas at different treatment times and powers. Both $N_2$ and $N_2/H_2$ reactive gases were used to functionalize the polymer surface prior to activation with Sn-Pd colloids and electroless metallization with copper. Results demonstrate that in any case plasma activation improves adhesion and homogeneity of the metallic deposit, moreover better results are obtained in pure $N_2$ and in $N_2$ with low amounts of $H_2$ (<20%). Adhesion is proposed to be improved by both chemical and mechanical contributions, due to the simultaneous incorporation of N-bearing polar groups and the modification of surface morphology: surface composition is determined by XPS, while modification of the morphology is confirmed by AFM and SEM imaging. Finally, according to the authors, RF plasma is less effective than microwave induced plasma at low treatment power, while the positive effect is comparable for both sources at high power (>50W).

Although in the abovementioned works plasma is reported to cause morphological modification to the polymer surface, this is usually proved to be minimal for reasonable plasma exposure time and power. For this reason low pressure NH$_3$ plasma has been proposed as activation process for the production of microelectronic devices, where excessive roughness is detrimental for the electrical circuit performance [67]. In this case epoxy resins, polyimide and their blends were treated with plasma resulting in increased adhesion of electroless copper deposits. A pre-activation process was developed that is based on chemical swelling followed by plasma treatment: it allows obtaining satisfactory adhesion levels with lower roughening with respect to an equivalent process based solely on chemical swelling. The chemical contribution to the total adhesion force is indeed quantified to be up to 50%, the remaining part being attributed to mechanical interlocking due to surface roughening after swelling.

More research has been focused on the application of plasma sources to the production process of flexible printed circuit boards based on polyimide films [68]. Following the fabrication scheme reported in Figure 1.15, it was possible to obtain selective deposition of copper by electroless plating with good adhesion levels and feature size in the order of the µm. At first PI is coated with spin-on glass (SOG) and subsequently with a photoresist (PR), which is developed allowing the selective etching of the SOG. According to the authors, copper is deposited on PI but not on the spin-on glass (SOG) since plasma treatment, performed in an ICP plasma reactor with $O_2$ followed by $N_2/H_2$, induces the formation of amine groups on the polymer but not on the glass. Therefore the Pd-based catalyst is
adsorbed preferentially on PI and the electroless process is catalysed and occurs only on the polymer, therefore generating metallic patterns that are the negative of the one of the SOG.

The interest in flexible printed circuits led to the development of simpler and faster processes for the production of patterned metallic deposits on polymeric films, in particular on polyimide (PI) [69,70]. With the aim of developing a roll-to-roll plasma printing and electroless metallization apparatus, the authors studied the effect of different plasma gas mixtures (at atmospheric pressure) on the adhesion and quality of galvanic deposits. Both whole area and patterned plasma treatment were performed using different DBD equipment: the first to determine Pd concentration after activation and adhesion of the metallic deposit by peeling, the second to state the applicability of the plasma printing process to patterned metallization. Air, pure nitrogen, nitrogen-diluted ammonia, APTMS, forming gas and forming gas/helium mixtures were used to pre-treat the polymer surface. Results indicate that the best results, in terms of adhesion of the electroless copper layer to the PI, are obtained with the He-diluted forming gas, although all the precursor gases, except air, gave satisfactory adhesion levels. The authors justify this behaviour considering that He is known to favour glow-like plasma, which is more homogeneous and effective in terms of surface functionalization. Adhesion levels as high as 1.2 N/mm were obtained with APTMS and 1.0 N/mm with He/forming gas, both values are higher than the requirement for flexible printed circuits. Results also indicate that, also with the precursor gas mixture containing He and forming gas, selectivity of metallization with electroless copper is not always obtained, therefore more work is needed to optimize the plasma printing and metallization process.

The growing interest in plasma pre-activation of polymers for the production of flexible electronics, justified by the possibility of increasing adhesion of patterned metallic deposits with minor roughness alteration, didn't cast a shadow over the environmental advantage of this pre-activation with respect
to chemical etching. Researchers indeed applied atmospheric plasma also were chemical etching is the universally accepted benchmark process, i.e. for ABS plating. In one case [71] an open-air system from Plasma Treat was used, operating at a frequency of 17 kHz and a high-tension discharge of 20 kV, with the aim of determining the entity and the durability of the modification induced by the treatment to ABS and PC samples. Results indicated that plasma treatment causes both an increase in the oxygen content at the surface, related to the incorporation of polar groups, and the creation of surface roughness. Moreover these effects were more evident for longer exposure times, i.e. for slower relative motion between the substrate and the plasma source, and affected more ABS than PC. A more recent work reports the application of plasma treatment to metallization of ABS with an electroless Ni-P bath [72]. A DBD equipment was used: it was operated at atmospheric pressure in air, with a plasma power supply that provides an output peak voltage of 15 kV and a maximum alternating current (AC) of 100 mA with a 20-kHz square wave.

![Figure 1.16](image)

**Figure 1.16** Scanning electron microscope images of the ABS surfaces: (a) with no plasma treatment, and (b)-(f) with plasma irradiation times 30s, 60s, 90s, 120s, and 180s, respectively [72].

Differently from most of the abovementioned works, in this case plasma treatment has not the main aim of introducing N-bearing functionalities but is performed to etch the surface in order to create a porous structure. Results indicate that surface roughness is increased with the formation of cavities that are similar to those obtained by chemical etching Figure 1.16, at the same time though wettability is increased due to the introduction of polar groups. Although the etching depth is shallower for plasma treatment than for chemical etching, the authors report that adhesion strength is higher in the first case. This can be justified considering the chemical modification of the polymer surface induced by plasma that pays a role in the adhesion mechanism.

Surface modification of polyimide by means of RF plasma at atmospheric pressure was also performed, with the aim of increasing adhesion of copper deposits, by a Korean group [73,74]. N₂, O₂ and a N₂/O₂ mixture with a 1:1 ratio were used as plasma gases. The samples were studied by means of FTIR, XPS, AFM, and contact angle measurements. Copper deposition was performed by means of a formaldehyde-free electroless bath, after activation with Sn/Pd catalyst. Results indicate that plasma treatment increases surface energy, with a greater effect for O₂ and the N₂/O₂ mixture. XPS and FTIR indicate that plasma causes the introduction of N and O containing functionalities in different proportions, depending on the precursor gas used. Considering the adhesion of the electroless copper, the best result is obtained after N₂ plasma, indicating that surface energy is not the only parameter affecting adhesion of the metallic deposit.
Finally Books can be found that are focused on adhesion [12], where significant portions are devoted to atmospheric and low pressure plasma treatment of polymers, or on the atmospheric pressure plasma treatment of polymers itself [10].

1.5 Innovative contribution

After shedding some light on the state of the art of plasma treatment and metallization of polymeric materials, the present work is aimed at further improving the knowledge regarding plasma modification and electroless metallization of polymers. While many of the cited studies make use of low pressure or controlled atmosphere discharges, in the present work two different open air and atmospheric pressure plasma sources are considered: a roll-to-roll DBD equipment for surface treatment of films and a plasma jet apparatus for tri-dimensional objects. This choice is determined by the desire of proposing processes that can be implemented at industrial scale. Therefore research activity has been focused not only on the fundamental characterization of plasma treated polymers and on electroless metallization, but it has been also devoted to the demonstration of the applicability of these two technologies to the production of products and devices. Although limited to the proof of concept, four different applications have been proposed: flexible concentrator mirrors for solar thermodynamic, oscillating diaphragms for micro-speakers, circuit breakers for low power systems and insulating foams for aerospace.

Finally, while most of the literature about atmospheric pressure plasma treatment and metallization is focused on commodity polymers (PE, PP, PET, ABS etc.), with the exception of polyimide for flexible circuit boards, in this work special polymers are considered including fluorinated (e.g. ECTFE and PVDF) and high performance aromatic (e.g. PEEK) polymers. Fluorinated polymers in particular, are known for their chemical inertness and low surface energy, which makes them hardly compatible with water based metallization processes. Moreover, while most of the literature is focused on the metallization of commodity polymers for aesthetic purposes (still with the exception of flexible circuit boards), in this work applications are considered where the metallic coating has a functional finality, e.g. thermal conduction and light reflection.

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Chapter 2
Characterization Methods

In this chapter the characterization techniques used through the research activity are described, in order to give a background and help understanding the data that will be presented afterwards. For sake of clarity, the techniques are organized into two main classes: the fundamental ones, i.e. the techniques used to understand the mechanism of plasma modification and electrochemical metallization, and the applicative ones, i.e. the techniques that are aimed at defining properties of the metal-polymer bilayer that are fundamental for a specific application.

2.1 Fundamental characterization techniques

In this first set are grouped all the techniques necessary to understand the several phenomena that affect the formation of metallic deposits on polymers after plasma treatment. First of all the modification of polymeric surfaces was investigated by AFM and XPS, in order to determine morphological and chemical changes respectively. Contact angle measurements were performed on plasma treated surface as an indirect measure of the modification induced by plasma treatment, moreover ageing studies were performed with this technique to understand the kinetics of hydrophobic recovery. SEM imaging was performed both on plasma treated substrates and after metallization for several purposes. Finally XRD was performed to determine the presence of preferential crystallographic orientations in the metallic deposits depending on the experimental conditions.

2.1.1 X-ray photoelectron spectroscopy

Once Einstein formulated the theoretical quantic explanation of the photoelectric effect in 1905, it was clear that the energy of the emitted photoelectron is strictly related to the solid from which it is
emitted. In 1914 Rutherford and co-workers demonstrated that the kinetic energy of the emitted electron is given by the difference between the X-ray energy and the binding energy of the electron itself. Another fundamental step towards the development of photoelectron spectroscopy was the observation of the line shift caused by chemical bonding. The first XPS spectra with high resolution were obtained by Siegbahn and his group in the 1950s. Their work continued in the following decades, especially focused on the analysis of core binding energies and their shifts due to chemical bonding. The acronym ESCA (electron spectroscopy for chemical analysis) was indeed coined by Siegbahn, who received the Nobel Prize in 1981 for its achievements in this field [75].

XPS is therefore based on a form of photoemission that consists in the ejection of an electron from a core level by an X-ray photon with sufficient energy. The energy of emitted electrons is analysed by the electron spectrometer and data are usually represented in a graph reporting signal intensity as a function of electron energy [76]. The kinetic energy of the photoelectron ($E_k$) is given by the difference between the X-ray photon energy $h\nu$ (where $h$ is the Planck constant and $\nu$ the frequency) and the binding energy of the core electron ($E_b$). The x-ray photon energy is determined by the source and it’s therefore known while the kinetic energy of the photoelectron is determined experimentally, therefore the binding energy is calculated as follows:

$$E_b = h\nu - E_k - \phi_s$$  \hspace{1cm} (2.1)

where $\phi_s$ is the spectrometer work function, as can be seen in Figure 2.1 [77]. Since the binding energy of an electron in a particular shell of an atom is unique, all the elements present on the surface of a sample, except H and He, can be identified and their relative composition can be determined.

The sampling depth of XPS is in the order of some nm, typically 10nm, from the top of the surface. This value is not determined by the penetration of X-ray photons, which is in the order of few micrometres, but from the inelastic mean free path of electrons, which is in the order of few tens of angstroms. Depth profiling can be performed with two distinct processes: if the thickness of interest is shallower than the penetration depth, angle resolved XPS is a valid and non-destructive method (Figure 2.2 ). On the contrary, if the thickness of interest is greater than the penetration depth, surface layers can be removed by sputtering with inert gases and XPS analysis is performed on the freshly exposed surface.

As previously anticipated, the binding energy of core electrons is specific for a given element but, at the same time, is perturbed by the presence of chemical bonds. It is therefore possible to determine the chemical environment surrounding the sampled element; the chemical shift can indeed be caused by several factors, including variations of the formal oxidation state, electronegativity of surrounding species, lattice sites, etc. For example the core level binding energy of the carbon atom increases proportionately with the electronegativity of neighbouring atoms. As a consequence it is possible to determine the substituents on the carbon, e.g. oxygen or fluorine, from the entity of the chemical shift.
and some quantitative evaluations can be performed based on the relative intensity of the shifted components.

This technique requires the sample to be irradiated under ultra-high vacuum (<10^{-9} torr) to increase the mean free path of electrons and photons. As a consequence only samples that are compatible to such levels of vacuum can be analysed. Moreover, for insulating samples, charge compensation needs to be performed to avoid the build-up of positive charges at the surface, which would negatively affect the measurement.

The basic XPS instrumentation consists of:
- a photon source to generate X-rays;
- an electron analyser to determine the kinetic energy of emitted photoelectrons;
- a detector to count the number of electrons (and therefore intensity);
- a data acquisition and processing system;
- an ultra-high vacuum system.

Ion guns can also be present in the vacuum chamber to perform sputtering for depth profiling. The X-ray source usually consists in a single X-ray gun with a twin anode configuration, providing AlKα or MgKα photons of energy 1486.6 eV and 1253.6 eV respectively [76]. A monochromator can be present and is especially useful for the acquisition of high resolution spectra, e.g. to resolve chemical states.

### 2.1.2 Contact angle measurement

As first noted from Young, wetting of a solid surface by liquid in air can be quantitatively described from the tangential angle of a droplet of said liquid at the liquid-solid-air interface. This angle (θ) is defined as the Young's or static contact angle and is the result of an equilibrium among three surface tensions:

\[ \gamma_{SV} = \gamma_{LV} \cdot \cos \theta + \gamma_{SL} \]  

Where \( \gamma_{SV} \) is the interfacial tension between solid and air, \( \gamma_{SL} \) is the interfacial tension between solid and liquid and \( \gamma_{LV} \) is the interfacial tension between the liquid and air (Figure 2.3). Besides the static contact angle also advancing and receding angles can be measured and their hysteresis gives information regarding the solid surface. Some fundamental requirements must be met in order to extract significant information, e.g. the surface energy of the solid, from the contact angle:

- The liquid and the solid surface must be physically and chemically nonreactive
- The solid surface has to be properly cleaned and the liquid must be pure, especially avoiding the presence of surfactants
- The solid surface should be homogeneous with respect to the dimension of the droplet of liquid, heterogeneities being at least one order of magnitude smaller than the droplet diameter.

![Figure 2.3](image)

**Figure 2.3** Schematic representation of the equilibrium of forces at the solid-liquid-air interface.

The most widespread technique to measure the contact angle is the optical based sessile drop method. As can be seen in Figure 2.4, a typical goniometer consists in the following components:

- An horizontal sample holder that can be manually or automatically actuated at least vertically (further degrees of freedom are optional);
- A light source pointed towards the sample holder;
- A CCD (charge coupled system) camera oriented towards the sample holder opposite to the light source;
- An automated dosing system, comprising one or more syringes, that allows dispensing a controlled amount of liquid, usually few µl, on the sample surface.

Depending on the requirements goniometers can be equipped with additional tools, e.g. high/low pressure chambers, high-speed camera systems etc.

![Figure 2.4](image)

**Figure 2.4** Example of goniometer.

As previously mentioned static contact angle is only one of the possible measurement methods. In this technique, the sessile drop is formed on the horizontal sample surface by dispensing the testing liquid using a motor-controlled dosing unit. Once the liquid droplet contacts the surface, some time is needed to reach the equilibrium condition (usually less than a second). Once equilibrium is reached, the static contact angle can be measured: at first the baseline needs to be defined, then the drop profile is approximated by the instrument software and finally the contact angle is calculated. This procedure needs to be repeated at least five times on the sample surface, in order to have significant data, and
variations in the measurement should be <2° if the surface of the sample is homogeneous. Since the results of this technique are easily affected by operator, some best practices need to be adopted:

- when using liquids with low boiling point, environmental controlled units should be introduced;
- The contact angle needs to be calculated only after the equilibrium is reached, this may imply the execution of preliminary tests to define the time necessary to reach equilibrium;
- The sessile drop can be formed in different ways, it can be dropped from the syringe onto the sample or the stage can be brought into contact with the pendant drop. Both processes have advantages and disadvantages, the former can cause distortion of the drop shape due to the dissipation of the kinetic energy accumulated during the fall, the latter suffers from the influence of needle shape;
- The volume of liquid should not be excessive in order to avoid drop deformation due to gravity;
- It is of paramount importance that drop profile elaboration is performed on high quality images: the liquid-solid boundary needs to be clear and focused with high contrast, so that errors related to profile fitting and baseline determination are minimized.

\[ \theta_{\text{min}} \]
\[ \theta_{\text{max}} \]
\[ \theta_{\text{adv}} \]
\[ \theta_{\text{red}} \]

Figure 2.5 Schematic representation of the two dynamic contact angle measurement techniques: tilting plate on the left and needle embedded sessile drop on the right.

The dynamic contact angle can be determined with two different techniques (Figure 2.5): the needle-embedded sessile drop method and the tilting plane method. In the former, a small sessile drop (1-2 µl) is dispensed on the sample, and then the drop volume is slowly increased up to a maximum volume of about 20 µl. The advancing experiment is concluded when the drop volume reaches its maximum, after that the liquid is withdrawn from the syringe and the volume is reduced, this is the receding part of the experiment. The tilting plate method has also been adopted to determine advancing and receding contact angle. In this method, the measurement is performed on a tilted stage when the liquid droplet starts sliding: the advancing angle is the contact angle at the leading edge, while the receding angle is that at the trail edge of the moving droplet. Although both methods have advantages and disadvantages from an experimental point of view, the tilting plate method is less reliable and the needle-imbedded sessile drop method is to be preferred.
Finally, the Wilhelmy plate method (Figure 2.6) provides an indirect force measurement technique to obtain interfacial surface tensions, static, advancing and receding contact angles. To be carried out the measurement also needs a high precision tensiometre. One limitation of this technique is the need of fabricating plates of the sample that must have the same characteristics on both faces and need to have well defined dimensions. Experimentally, the sample is dipped in the liquid so that the solid-liquid-air interface is formed. A number of forces acts on the sample, namely:

\[ F_T = F_w - F_b + F_g \]  \hspace{1cm} (2.3)

Where \( F_T \) is the force measured by the tensiometre, \( F_w \) is the wetting force, \( F_b \) the force of buoyancy and \( F_g \) the force of gravity. The wetting force is given by:

\[ F_w = \gamma_{LV} \cdot L \cdot \cos \theta \]  \hspace{1cm} (2.4)

Where \( L \) is the total length of the three-phase interface. If the instrument is calibrated so that \( F_g \) is set to zero, the contact angle (\( \theta \)) can be calculated easily without the uncertainty related to operator-induced errors, indeed:

\[ F_T = F_w - F_b = \gamma_{LV} \cdot L \cdot \cos \theta - S \cdot h \cdot \Delta \rho \cdot g \]  \hspace{1cm} (2.5)

Where \( S \) is the cross sectional area of the sample, \( h \) the immersion depth and \( \Delta \rho \) the difference between the density of the liquid and the density of air. This method also allows the determination of advancing and receding contact angle if the plate is slowly immersed or withdrawn from the surface.

The measure of contact angle is usually aimed at determining the surface tension of the sample. It is first of all important to distinguish between surface tension and surface energy. For a liquid these two entities are coinciding, while for a solid they are distinct quantities: Surface energy (J/cm²) is the reversible work necessary to form a unit area of surface at constant equilibrium density of surface atoms, while surface tension (N/m) represents the mechanical work needed to deform a surface with fixed composition [78]. Several methods have been proposed that allow to determine this property of the solid basing on the contact angle value. Among the others, these methods include the Zisman’s, the Fowkes’s and the equation of state methods:

- Zisman method: this empirical method is based on the linear relationship between the cosine of the contact angle (\( \cos \theta \)) and the surface tension of the liquid (\( \gamma_{LV} \)) used to wet the solid sample. The intercept at \( \cos \theta = 1 \), which implies the complete wetting of the substrate, is defined as the critical surface tension (\( \gamma_C \)) of the solid. \( \gamma_C \) is empirically found to be very close
to the solid surface tension. It is important to point out that the Zisman is only valid for low surface energy surfaces and alkane solvents, where van der Waals force is predominant.

- Fowkes and Owens–Wendt–Rabel–Kaelble (OWRK) methods: Fowkes was the first to overcome the limitations of Zisman method considering that surface tension of a solid is the result of a sum of independent components, as dipole-dipole interactions, hydrogen bonding etc. In the original Fowkes method only the dispersion component of the surface tension, which is related to London dispersion forces, was considered, resulting in:

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2 \sqrt{\gamma_{SV}^d \cdot \gamma_{LV}^d}$$

Where $\gamma_{SV}^d$ and $\gamma_{LV}^d$ are the dispersive components of the solid and of the liquid surface tensions respectively. The OWRK method is implemented including H-bonding, which is identified in the non-dispersive (or polar) component of the surface tension. This results in:

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2 \sqrt{\gamma_{SV}^d \cdot \gamma_{LV}^d} - 2 \sqrt{\gamma_{SV}^p \cdot \gamma_{LV}^p}$$

This method is also referred to as the two-liquid method, since the contact angle needs to be determined with two different liquids (one completely apolar and one having a polar component) to calculate the surface tension of the solid.

### 2.1.3 X-ray powder diffraction

There are three different types of interaction between x-rays and matter, two are related to inelastic scattering while one to elastic collisions between x-rays and electrons. Photoionization is an example of inelastic scattering that implies the emission of an electron due to energy and momentum transfer by the electromagnetic radiation. Also in Compton scattering energy is transferred to electrons that anyway are not emitted. Finally x-rays can be scattered elastically by electrons, resulting in Thompson scattering, which is the base of structural investigations techniques by x-rays [79]. X-ray diffraction is essentially an elastic scattering phenomenon which involves a high number of atoms; since atoms in a crystal are periodically arranged, a constructive interference is built in some specific directions.

The diffraction of light had been understood before the discovery of X-rays, visible light was indeed known to diffract when encountered regularly spaced objects, having periodicity in the same order of magnitude as the wavelength of light. The firsts to study X-ray diffraction were Max von Laue and William Bragg, to whom the basic laws governing this phenomenon are due. Bragg’s law states a condition that needs to be satisfied in order to have constructive interference among the waves scattered by atoms in a crystal. This law can be applied to both atoms laying in the same crystal plane

![Figure 2.7 Schematic representation of scattering from atoms in the same plane (a) and in different crystalline planes (b).](image-url)
or in different planes, as can be noticed in Figure 2.7. In the first case the ray scattered by the atom in position A has the same phase as the ray scattered by the atom placed in position B, the length AD is indeed equal to CB, therefore the two waves are in phase also after scattering. If different crystalline planes are considered, Figure 2.7 (b), there is a finite difference in the length covered by the x-ray diffracted by the atom in A and the one diffracted by the atom in B. This length is equal to CB+BD = 2dhkl senθ, where dhkl is the inter-planar spacing. The Bragg’s law states that, in order to have constructive interference, the path length difference must be an integer multiple of the wavelength, i.e.:

\[ n\lambda = 2dhkl \text{sen}\theta \]  

(2.6)

Where \( n \) is an integer and \( \lambda \) is the wavelength. In other words, this equation states that the incident and diffracted beams are coplanar with the normal to the lattice planes and inclined at 90°-θ, where θ (the Bragg angle) is determined by the wavelength and the interplanar spacing. In practice a number of planes is contributing to the scattering process since the X-ray beam size is larger than the interatomic distance. This is the reason why, differently from optical reflection, diffraction needs the Bragg law to be satisfied: only for specific θ values the interference is constructive and therefore a finite signal can be detected.

The term x-ray powder diffraction includes the analysis of all the samples that are composed of multiple crystalline grains, e.g. bulk samples, coatings and powders of crystalline materials [80]. In a randomly oriented polycrystalline sample, irradiated by a monochromatic X-ray beam, a high number of crystallites is always correctly oriented so that the Bragg law is satisfied. The result of irradiation of a polycrystalline sample is the formation of the so-called Debye cones (Figure 2.8), each relative to a specific crystalline plane (h,k,l) that satisfies the Bragg law at a specific angle \( \theta_{h,k,l} \).

![Figure 2.8](image) Schematic representation of the generation of Debye cones due to scattering from a polycrystalline sample and resulting bidimensional diffraction pattern.

The basic XRD instrument is usually composed by [80]:

- An XRD source: the most common source is the X-ray tube where electrons are thermoionically emitted by a filament and hit an anode. The anode, in turn, emits x-rays that are used to characterize the sample. Two kinds of X-rays are emitted: the braking radiation, resulting from the gradual energetic loss of electrons, and a second radiation, which, differently from the previous, has a specific wavelength. The resulting emission spectrum is therefore composed of a background noise and a sharp peak associated to the specific emission of the target. The anode is usually water-cooled to avoid melting and the whole system is under vacuum to avoid contaminations and allow sufficient free path to electrons.
- Filters and monochromators: in order to clean the emission of the X-ray tube, i.e. make it as monochromatic as possible, two different solutions can be adopted, i.e. filters and monochromators. The first usually consist of thin sheets of a material that absorbs all the
radiations below a certain wavelength. A monochromator, on the other end, consists of a single crystal that is oriented so that only a specific wavelength is diffracted. Therefore is easy to understand that while the latter allows obtaining a monochromatic signal, the former only helps in improving the signal quality by reducing the intensity of the unwanted components.

- A goniometer: in the Bragg-Brentano configuration, the goniometer is responsible for the correct relative positioning of sample and detector with respect to the X-ray source. This configuration is also referred to as the $\theta-2\theta$ configuration since the sample is placed on a sample holder, which is kept at an angle $\theta$ with respect to the source, while the detector is located at $2\theta$. Therefore while the sample holder is rotated at speed $\dot{\theta}$ the detector revolves at speed $2\dot{\theta}$.

- A detector: originally, detectors consisted in photographic films. Nowadays gas detectors are the most used. These rely on the measurement of electrical currents produced by the ionization of a gas by X-rays. Several architectures are present, including position sensitive detectors, which allow measuring both the number of electrons and their position, thus reducing the acquisition time with respect to punctual detectors.

- Electronics: responsible for signal amplification and interface with the elaboration software.

The result of data elaboration is a spectrum where intensity, usually in counts per second, is reported as a function of the diffraction angle ($2\theta$). The qualitative pattern of the spectrum is specific for each crystal system, therefore the components of unknown samples can be determined (only relative to the crystalline portion) basing on the position of peaks and their intensity. Further information, as the presence of residual stresses [81] or the crystallite size, can be deducted but need further data elaboration and can easily lead to misinterpretation, if the models are not employed correctly.

### 2.1.4 Scanning electron microscopy

The earliest demonstration of this imaging technique, which makes use of electrons as sampling beam, was given by Knoll in the 1930’s. Since then, the instrument has been highly improved and its birth can be considered as a major breakthrough in the study of microstructure and, partly, composition of bulk materials [82].

As mentioned, SEM makes use of electrons to generate an image of the superficial portion of a sample. The interaction of the primary beam of electrons with the sample generates a wide range of signals that can be used to gather information, e.g. X-rays, backscattered and secondary electrons. This technique makes use mainly of backscattered and secondary electrons. The selection of electrons as probing radiation is related to the feature-size that can be imaged, i.e. the shorter the wavelength the higher the resolution, with the most advanced SEMs having resolution better than 1nm. If compared to transmission electron microscope (TEM), this technique allows analyzing samples of relatively large dimension, up to the cm range, with minor sample preparation operations. If compared to optical microscopy, this technique allows achieving a higher resolution with a larger depth of focus.

Neglecting added functionalities, two main classes of scanning electron microscopes can be identified depending on the operative pressure, namely low pressure and environmental or variable pressure systems. The basic components are anyway common to both kinds of instrument and include [82,83]:

- An electron Source: electron beams are produced by applying a high voltage to a filament, which can be either a thermionic emitter or a field emission source. An important parameter that is common for both electron sources is the brightness ($\beta$), which is given by the current density (in A/m$^2$) per solid angle (in steradians):
\[ \beta = j_b / (\pi \alpha^2) = 4i_b / (\pi^2 d_0 \alpha^2) \]  

Where \( j_b \) is the current density, \( i_b \) is the emission current, \( \alpha \) is the convergence semi-angle and \( d_0 \) the crossover diameter of the beam. Thermionic emission sources usually consist of a V-shaped tungsten filament. The filament is resistively heated until electron energy exceeds the work function and electrons are therefore emitted. Field emission sources are usually based on the excitation of a single crystal of lanthanum hexaboride (LaB\(_6\)), which allows achieving higher brightness than tungsten. Due to the smaller emitting area, better resolution can be obtained with this source with respect to the thermionic one.

- Lenses and apertures: Lenses are used, to shape and focus the electron beam, that usually consist of copper wire windings inside a soft iron shell. Electrons flowing inside the magnet are subjected to both radial and circumferential forces that are stronger if the current in the copper windings is increased. While lenses determine the spot size by focusing electrons, apertures determine the angular range of electrons that are allowed to travel on to the objective lens by blocking part of the primary beam. Reduction of spot size by means of apertures determines indeed a reduction of the beam current.
- Coils for scanning the beam on the sample.
- Control electronics to modulate the source voltage.
- A detection and acquisition system: the interaction of the primary electron beam with the sample generates a wide range of signals; each of them is originated within a specific region of the sample sub-superficial volume, as shown in Figure 2.9. The extension of this “interaction volume” is also dependent on the acceleration voltage of the electron beam and on the atomic number of the atoms composing the sample. The lower the acceleration voltage and the higher the atomic number, the lower the penetration depth. The detection and acquisition system should be able to collect all the available information coming from a selected number of signals emitted from the sample due to the interaction with the primary electron beam.
- A monitor to display information.
- A vacuum system for source, column and specimen chamber: this is needed to avoid contaminations and scattering of electrons composing the primary beam.

![Figure 2.9](image.png)  

**Figure 2.9** Schematic representation of the interaction volume of the primary electron beam[82].
Different information about the sample can be gathered depending on the signal that is collected at the detector. The fraction of primary electrons that, due to collisions with the atoms composing the sample, are turned to backscattered electrons, depends both on the atomic number of the material composing the sample and on the tilt angle of the sample. In particular this is higher if the atomic number is higher and is lower for flat surfaces with respect to sharp edges or sloped features. This two relationships have important consequences: the first allows determining differences in composition (if the atomic number of the atoms is different enough) of the sample, with heavier elements appearing brighter. The second allows distinguishing topological features by contrast.

Secondary electrons are loosely bound valence (or conduction) electrons that are excited by the primary beam and are able to leave the sample, after losing some energy due to inelastic collisions. Secondary electrons have lower energy than backscattered ones and their ratio with respect to the number of primary electrons is almost insensitive to the atomic number. Due to their low energy they are emitted only from the outmost portions of the sample and are therefore used mainly for morphological analysis. As for backscattered electrons the signal is stronger at sharp edges than from flat surfaces.

Finally the excitation induced by the primary beam can be relaxed by the emission of specific X-rays. This signal is particularly important for the determination of the atomic composition of the sample, which is usually addressed to as microanalysis. The most common form of microanalysis is the energy dispersive X-ray spectroscopy (EDX or EDS) and the determination of the chemical composition of the sample is possible since each element is characterized by a very precise emission energy.

Since the sample is bombarded by electrons during imaging, SEM has some limitations. Insulating samples need to be coated with thin conductive layers in order to allow charge drain, otherwise electron bombardment would cause charge build-up with consequent imaging issues and sample damaging. Moreover, since in low pressure systems the sample chamber is also under vacuum, samples must be able to withstand low pressure without the generation of particles or emission of volatile compounds. Atmospheric systems allow working at higher pressure therefore resulting in less stringent requirements for sample resistance to vacuum.

2.1.5 Atomic force microscopy

Differently from other microscopy techniques, AFM doesn’t make use of focused electrons or light to image the surface of a sample, but interacts with the sample by means of a sharp probe and builds a map of the height of the sample surface. The origin of AFM is strictly connected to that of scanning tunnelling microscopy (STM) and both are referred to as scanning probe microscopies, due to their similarities. AFM was indeed ideated in 1986 by making some modifications to an STM apparatus [84], and showed advantages with respect to its "parent technique" since it can be operated, as will be shown later, on a much broader range of samples with loose experimental environment limitations.

AFM is based on the attractive and repulsive forces that act on two bodies when they are brought into contact or very close to contact. The core of the instrument is a sharp probe mounted near to the end of a flexible cantilever; the probe is scanned on top of the sample and allows determining the topological features of the surface, thanks to the monitoring of cantilever deflection. Once scanning is concluded a tri-dimensional image of the sample is generated with high resolution. The cantilevers are usually V-shaped and the probe is either a square-based pyramid or a cylindrical cone, the most common materials being silicon and silicon nitride. The upper surface of the cantilever is also usually coated with a thin layer of a highly reflective metal, usually Au or Al. The tip-sample distance along the z-axis (usually orthogonal to the sample holder) is controlled by means of a piezoelectric transducer.
while the cantilever deflection is determined by a laser beam that, after being reflected by the uppermost surface of the cantilever, hits a position sensitive photodetector. Therefore a change of the position of the laser spot on the photodetector is associated to a specific deflection of the cantilever [85]. A schematic representation of the basic AFM setup is shown in Figure 2.10.

![Figure 2.10 Schematic representation of the AFM setup.](image)

To go in further detail, the main components of an AFM are the microscope stage itself, control electronics and a computer [84].

The stage includes the scanner, the sample holder, a force sensor and may include an integrated optical microscope. To avoid the presence of vibrations, which could jeopardize the measurement, the stage is usually supported on a vibration insulation platform. The scanner allows to raster the sample and therefore is responsible for the relative motion of sample and probe in the three dimensions (x-y-z). Usually, a coarse movement control system is also present to place the sample and probe in the correct position to start the imaging process. Two different configurations can be identified, depending on the modality of scanning: sample scanning, where the sample is mounted on a x-y-z scanner the probe is fixed, and probe scanning where the opposite occurs; the first being more simple and the second more versatile, but complex to be designed. While coarse movements are performed by means of mechanical actuators, fine movements are, in the great majority of cases, performed by means of piezoelectric actuators.

Due to the reduced dimension of the probe tip, the force sensor must be able to measure very small forces. As previously mentioned, the most widely used force sensor is the optical lever. Once the laser beam is reflected from the backside of the cantilever, the beam spot hits a position-sensitive photodetector; when the deflection of the cantilever is modified by the interactions with the sample being analysed, this setup amplifies the small displacement of the tip with a large displacement of the beam spot on the photodiode. The force acting on the cantilever is determined by the change in light intensity detected by each of the four quadrants (A, B, C and D of Figure 2.10) of the photodetector.

Control electronics are mainly responsible for:

- Generating scanning signal for the piezoelectric x-y motion system;
- Generate an output for the piezoelectric z motion system after receiving an input from the force sensor;
- Collect all the signals to be displayed on the computer.
Finally, many imaging modes are available for AFM, which can be preferred depending on the sample and on the information that need to be acquired. It is first of all important to consider the qualitative force regimes acting on the probe tip and the sample (Figure 2.11). When the probe is sufficiently far from the sample, no interaction occurs between the two and the force is nil. As the tip approaches the sample, Van der Waals interactions start to pull the tip towards the substrate, therefore attractive forces are present. Finally, when contact is made, repulsive forces are generated by the interaction among electron shells of the atoms composing sample and probe. The different imaging modes fall in different areas of the force-relative position graph [84,85] (Figure 2.11):

- **Contact mode**: in this imaging mode, sample and probe are always in contact, forces are therefore repulsive. This is the simplest operative mode and allows obtaining high resolution images of the surface. Two variations exist for this mode: constant force and constant height. In the first case the z-position of the probe is continuously modulated so that the force is constant, while in the second the z-position is constant and the force is measured. In the vast majority of cases constant force mode is preferred but can result in higher resolution on extremely flat samples. Contact mode is usually used on hard and flat substrates due to its simplicity of operation. Drawbacks include lateral forces acting both on sample and probe, damaging of the tip and deformation of the substrate, leading to a reduction in resolution due to the increased surface of contact.

- **Non-contact oscillation mode**: this imaging mode is performed keeping the probe very close to the surface, so that only attractive forces are present between tip and sample. The cantilever is usually oscillated at (or very close to) its resonant frequency, when the force of interaction between the sample and the tip changes, due to a variation in the relative distance, the frequency or the amplitude of oscillation are affected. Imaging is performed maintaining the cantilever at a fixed distance from the sample, exploiting variations of frequency or amplitude of the oscillation. This operative mode can be used for imaging almost any sample but it's usually used less often than intermittent contact mode, when working in ambient conditions. In these conditions a contamination layer is usually present, giving rise to capillary forces that affect the measurement. In order to have reliable results, imaging should be performed with the tip constantly immersed in the contamination layer, which requires a stiff cantilever and much care. This operational mode can be operated inside liquids and is able to give atomic resolution in ultra-high vacuum.
• Intermittent-contact oscillation mode: the working principle of this mode is basically same as the previous, but the tip-sample interactions involve all the force regimes since the tip oscillates from a no-interaction distance to contact and therefore repulsion. In this mode, the tip periodically contacts the surface therefore it can be damaged, but at the same time lateral forces are almost eliminated thanks to the vertical motion of the tip and the effect of contamination layer is reduced since the tip passes through it. Therefore this technique is preferred to non-contact oscillation since it can be easily operated in air, but its application in fluids is limited due to the difficulties in the mechanical excitation of the cantilever. Finally this imaging mode is not usually performed in vacuum.

Many others AFM operative modes are present, giving non-topographic information and therefore usually referred to as spectroscopic modes. Among the most common is for example force spectroscopy. This mode requires the x-y position to be fixed and the z position to be varied so that the tip is brought into contact and then retracted to the no-interaction zone. It’s therefore possible to monitor specific interactions between the substrate and the tip, which can be functionalized with a wide range of molecules.

### 2.2 Applicative Characterization techniques

In order to validate the feasibility and the applicability of plasma treatment and electrochemical metallization to special polymers for the proposed applications, specific characterizations were performed. Each characterization technique was selected to determine whether the studied metallization process allows obtaining a specific property for the metal-polymer assembly. It is important to keep in mind that this work is not aimed at defining a complete manufacturing process for the final product, but is meant to demonstrate the feasibility of a given device. Therefore only the main properties were characterized for each application, namely: UV-VIS-NIR light reflection was measured, by spectrophotometry, on samples for solar concentrator mirrors, IR thermography and micro-tensile testing were performed on samples for the micro-speaker application. Other tests have been performed but they are not considered characterization techniques by the author, therefore they will be described in more detail in chapter three.

#### 2.2.1 UV-VIS-NIR spectrophotometry

The term spectrophotometry is used to identify the quantitative measurement of the optical properties of materials in a wide range of wavelengths including ultraviolet, visible and near-infrared radiations. Several phenomenological properties of the material can be identified with this technique, including spectral reflectance, transmittance, absorptance, emittance, scattering and fluorescence. Other intrinsic properties of the sample can be determined, including its refractive index and the extinction coefficient.

The first automated spectrophotometer was developed by Hardy and his colleagues between 1926 and 1928. In the following years, significant improvements were introduced in the instrument, including the creation of multi-wavelength apparatuses in the 1970s and the introduction of the diode array spectrophotometer in 1979.
In its simpler form a spectrophotometer is composed by three parts: a source, a sample holder and a detector [86]. The source is responsible for the generation of the electromagnetic radiation, which must cover all the wavelengths of interest for the experiment, for example, when characterizing materials for solar energy applications, spectrophotometric experiments extend from 200nm to 2500nm. Examples of light sources include tungsten filament lamps and xenon flash lamps. The light emitted by the source can afterwards be monochromated by means of different elements, the most common of which is the diffraction grating. This component allows splitting a polychromatic light beam into its components at different angles, depending on their wavelength. The detector is designed to be sensitive over, at least, a portion of the spectral range of interest; it is indeed common to have multiple detectors for a single instrument so that a broader spectral range can be covered. The detector needs to produce an electric signal when hit by the light beam, its intensity being proportional to the light intensity; examples of photodetector materials include silicon and gallium nitride. When the sample to be analysed is a fluid, this needs to be contained into a cuvette, the sample holder can usually be adapted to allocate both solid samples and cuvettes, containing fluids.

As depicted in Figure 2.12, three main instrumental configurations can be identified [87]:

- **Single beam spectrophotometers** are the simplest and are usually used for routine laboratory measurements at a single wavelength. In this configuration only one light beam is used to characterize the sample. It is therefore necessary to define both the intensity of light hitting the sample and the reference transmittance (or absorbance) value of the sample holder, if present. This implies performing a further measurement without the sample, e.g. for samples in solution, this means obtaining the reference on the cuvette and eventually the solvent.
Split and double-beam spectrophotometers have an internal reference that allows performing the measurement on the sample and on the reference simultaneously. The difference between these two set-up is that in the double beam instrument only one detector is present, while in the split set-up two detectors are present; therefore in the first case sample and reference signal are detected alternatively, while in the second case they are detected simultaneously. The double beam set-up makes use of a chopper that usually oscillates or vibrates at about 50Hz reflecting the beam alternatively either on the sample or on the reference. The split beam spectrophotometer makes use of a beam splitter, therefore the intensity of light hitting sample and reference is half the original value.

The schematic representations, reported in Figure 2.12, are representative of experiments performed to measure transmittance, the principle is the similar also when reflectance needs to be measured. As stated previously, the spectrophotometer can be used to define a wide range of phenomenological and intrinsic properties of solid and fluid samples. In this thesis work the instrument was used mainly to determine transmittance, specular reflectance and diffuse reflectance, within the solar spectrum. Transmittance, as the other two phenomenological quantities, is comprised between 0 and 1; it is the fraction of light that is able to go through the sample and reach the detector, it is therefore calculated as the ratio between the detected light intensity and the intensity of light hitting the sample [88]. In this apparently simple measurement, it is necessary to consider contributions from absorption and scattering, therefore several experimental procedures have been proposed to determine the real transmittance of the sample. Moving to reflectance measurements, two limiting cases can be met: a parallel beam of light that hits the sample can be either reflected specularly or reflected uniformly in all directions of the hemisphere. In the first case the sample has a perfectly polished surface acting as a mirror, in the second case the surface is ideally matte. In practice these two ideal conditions are never met, but samples can show intermediate properties. The determination of these two reflection modes implies the utilization of different experimental setups [89,90]: for specular reflectance various methods, and therefore instrumental configurations, are adopted, including the V-W, the V-N and the goniometer-based methods. When diffuse reflectance needs to be measured, integrating spheres are adopted, which allow to collect and therefore detect the light reflected by the sample in all the directions.

2.3 IR thermography

IR thermography can be considered by all means a non-destructive testing technique [91]. Since the availability of commercial infrared cameras in the late 1980s, its potential as non-destructive quality control process has been constantly increasing. At the same time much research activity is being performed in this field to improve image processing and the potentiality of this technique as inspection method [92]. William Herschel could be somehow considered the father of this technique: after separating the components of visible light with a prism and measuring the temperature with a glass thermometer, he noticed that the maximum increase of temperature occurred beyond the red band where no radiation was visible, i.e. in the infrared.
Figure 2.13 Photograph and correspondent IR thermograph of a PE pipe with the presence of simulated imperfections [91].

Today many instruments can be used as temperature sensors in several conditions, examples include, for example, the common glass thermometer, the thermocouple and radiation detectors. This last category is the most common for non-contact temperature measurement; this implies advantages since there’s no perturbation of thermal equilibrium and some disadvantages, related to reflections and differences in the emissivity of different surfaces. When adopted as inspection technique, as in Figure 2.13, IR thermography can be used according either to the active or to the passive approach. In the first case the material to be tested is heated above room temperature by an external heat source, this is the example of vibro-thermography, where the induction of vibrations causes heat to be released by friction where defects are present. In the second case the piece to be imaged is spontaneously above room temperature, examples include quality control in arc welding or in the production of metals, determination of thermal insulation of building envelopes, detection of gas leaks, etc.

Detectors for IR imaging can be divided into two large families: thermal and photonic detectors [92]:

- In thermal detectors, the radiation is absorbed and causes a temperature variation of the detector itself. The most used detector falling in this class in the pyroelectric vidicon, in which a target releases charges due to localized heating, the image is therefore read by scanning an electron beam on the target. Advantages of this kind of detector include wide spectral response and no need for cooling. Disadvantaged rely on the fact that the detector is only sensitive to temperature variations, therefore a mechanical chopper is needed to generate an absolute temperature reference, causing on the other end flickering of the image (which can be corrected by means of electronics). Moreover only a small temperature range can be observed, detectivity is lower than in photonic detectors and the life span of the detector is short, especially if a given pattern is observed repeatedly.

- In photonic detectors, electronic states of a semiconductor are excited by the absorption of photons. If the energy of an incident electron is sufficient to release an electron, detector conductivity or output voltage (depending on the semiconductor) is increased. In order to have detection, the energy of the photon must be sufficient to cause the excitation of electrons in the semiconductor. The advantages of this class of detectors include excellent detectivity and high reliability on the acquisition of quantitative images. Disadvantages include high cost, need to cool the detector to cryogenic temperature and slow response time.
An IR camera is not a thermometer but a radiometer, this implies that the information collected can be translated into temperature values only if some hypotheses are met and if some parameters are known. A brief overview of these hypotheses and parameters is given hereby [92]. The black body serves as reference for thermal emission of solids and is capable of absorbing totally all incident radiation as well as re-emitting the radiation uniformly in all directions. If thermal equilibrium is reached, at temperature \( T(K) \), the spectral radiance \( N_{\lambda,b} \) is given by:

\[
N_{\lambda,b} = \frac{2hc^2}{\lambda^5} \cdot \frac{1}{\exp\left(\frac{hc}{\lambda kT}\right) - 1}
\]  

(2.8)

Where \( h \) is the plank constant, \( c \) the velocity of light, \( k \) the Boltzmann’s constant and \( \lambda \) the wavelength of the emitted radiation. Real objects are not usually identified as black bodies since they don’t absorb (and re-emit) all the electromagnetic radiation. The emissivity of a body, \( \varepsilon \), is therefore defined as the ratio between its spectral radiance and that of the black body. Objects whose emissivity doesn’t depend on the wavelength are called grey bodies, while for coloured bodies the emissivity depends on the wavelength. Therefore for coloured bodies the spectral radiance can be defined as:

\[
N_{\lambda} = \varepsilon N_{\lambda,b}
\]

(2.9)

Moreover, for opaque objects, emissivity can be related to reflectivity, \( \rho \), for incident isotropic radiation the following holds true:

\[
\varepsilon = 1 - \rho
\]

(2.10)

The last two equations highlight the issues relative to surfaces with low emissivity, which emit weakly and tend to reflect incident radiations to the detector, causing serious imaging criticalities. To conclude, the radiance received by the camera \( N_{\text{cam}} \) is expressed by:

\[
N_{\text{cam}} = \tau_{\text{atm}} \varepsilon N_{\text{obj}} + \tau_{\text{atm}} (1 - \varepsilon) N_{\text{env}} + (1 - \tau_{\text{atm}}) N_{\text{atm}}
\]

(2.11)

Where the first term is relative to the object, the second to the surrounding environment and the third to the atmosphere and: \( \tau_{\text{atm}} \) is the transmission coefficient of the atmosphere in the spectral range of interest, \( N_{\text{obj}} \) is the radiance from the surface of the object, \( N_{\text{env}} \) is the radiance of the surrounding environment considered as a black body and \( N_{\text{atm}} \) is the radiant of the atmosphere, supposed constant. This equation can be simplified and \( N_{\text{cam}} \) can be considered, in first approximation, equal to \( N_{\text{obj}} \) if the transmission coefficient of the atmosphere is considered equal to one as well as emissivity and if there is no high temperature object close to the inspection position. Once this is clear, equations exist that allow correlating the radiance received by the camera with the temperature of the object. When extracting quantitative thermal information from IR imaging, it is necessary to consider than many sources of error are present, including: aberrations of the optical system, non-uniform spectral response of the instrument, distortions induced by the image forming process of the instrument, self-emission of the detector (only for non-cooled systems) and Narcissus effect linked to the reflection of the detector in the optics.

### 2.4 Micro-tensile testing

With the development of micro-structures, e.g. MEMS, the characterization of the mechanical properties of thin films is of paramount importance. Due to the reduced dimension of samples, traditional mechanical characterization techniques were not suitable; for this reason, starting from the 1990s, many efforts have been produced to develop characterization equipment and procedures that could be applied to micro-structures, in particular thin films.
Concerning micro-tensile testing, several geometries and technological solutions have been proposed from different research groups. The basic components of a micro-tensile testing machine are the same as a traditional tensile machine; the difference lies in the need of minimizing friction as much as possible, due to the reduced magnitude of the forces measured by the system. The main components of a tensile test machine are:

- **Mechanical Frame and Grips:** due to the small dimension of samples, and therefore the small magnitude of the forces that need to be measured, this portion of the instrument must insure that friction is minimized as much as possible. It has been solved according to different approaches, which include the utilization of air-bearings [94] or the mounting of the sample inside a suspended elastic frame with known compliance [93].

- **Displacement actuator:** displacement of the free end of the mechanical frame is usually induced by means of precision translation stages, as dovetail slides, actuated by suitable motors with reduction gears to allow low and precise displacement rates [93,94].

- **Load sensor:** the determination of the applied load is usually not complicated and performed by means of commercially available load cells, which provide a voltage output that is proportional to the applied load.

- **Strain sensor:** measurement of the applied strain is another critical point of this characterization technique. The interferometric strain/displacement gage (ISDG) is usually adopted for this purpose since has many suitable characteristics [93–95]: it is non-reinforcing and non-contacting, i.e. it is a non-contact measurement technique, which is important considering the small dimensions and the reduced stiffness of the sample. In other words a strain sensor attached to the sample would cause both alterations in the measured stiffness and would be practically difficult to apply. Finally this method allows performing measurements with high precision and resolution.
An example of instrumental apparatus used in the literature is given in Figure 2.14. The theory of traditional tensile testing holds true also for micro-tensile testing and the information that can be gathered with this technique are the same. Tensile testing allows to determine some of the most used mechanical information of a material, including yield strength and deformation, failure stress and deformation and elastic modulus, moreover other information regarding the material can be collected observing the fracture surface and mode and the stress-strain curve. During tensile testing a sample is placed and gripped between two crossheads, one fixed and one adjustable, which are displaced at a controlled speed. During this displacement the sample is stretched and both the applied load and its deformation are monitored. Displacement and load are therefore converted into stress strain curves, three examples are shown in Figure 2.15, where engineering (or nominal) stress and strain are calculated as follows:

$$\sigma = F/A_0$$  \hspace{1cm} (2.12)
$$\varepsilon = \Delta L/L_0$$  \hspace{1cm} (2.13)

Where $F$ is the tensile force, $A_0$ the initial cross-sectional area of the specimen, $L_0$ the initial gage length and $\Delta L$ the variation in gage length. From the stress-strain curve many information can be determined, including [96]:

- Elastic modulus: the initial portion of the curve is characterized by a linear correlation between stress and strain. If the sample is maintained in this condition during elongation, once the load is removed, the deformation returns to zero; this deformation is therefore reversible and is referred to as elastic. On the other end, plastic deformation occurs if the deformation is not recovered after unloading. The Elastic modulus is determined in the linear portion of the curve, and is given by:

$$E = \sigma/\varepsilon$$  \hspace{1cm} (2.14)

- Yield points: the yield point is defined as the stress value that causes the material to undergo plastic deformation. In other words for stress values lower than the yield point, the material is in the elastic deformation regime, while above the yield point in the plastic deformation...
regime. In some cases, as in the dash-dotted line in Figure 2.15, the so-called lower yield strength is considered due to the dependence of the upper yield strength on the testing conditions. The ultimate tensile strength is the highest stress that the material can withstand before failing; brittle materials usually have tensile strength but not yield strength.

- Ductility: two methods are usually used to define the ductility of a sample. The first is the measurement of the percent elongation, which coincides with the percent value of the strain at failure. Care should be paid if to consider only the plastic deformation at yield, since in certain cases, e.g. elastomers, the elastic deformation can be relevant. The second common method to collect information on ductility is to measure the percent reduction of cross-sectional area of the specimen at yield.

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Chapter 3
Experimental Procedures

This chapter defines the experimental procedures adopted for the thesis project. After a brief overview of the polymers studied during this project, the description of activities is organized and divided into two main portions: a first part of this chapter is focused on plasma treatment and metallization, both from the point of view of sample preparation and characterization. The second part of the chapter is focused on the applications, precisely on the tests performed to validate the samples. It is to be kept in mind that testing, specific for each application, is performed on the samples obtained according to the experimental procedures defined in the first part of this chapter.

![Figure 3.1 Schematic representation of the chemical structure of PEEK.](image)

KetaSpire® PEEK (polyetheretherketone) is one of the highest performing semi-crystalline thermoplastics available today. Due to its outstanding mechanical properties it is used to replace metals in severe end-use applications, where chemical resistance needs to be associated to good mechanical properties even at high temperatures, e.g. piston parts, compressor plate valves and bearings. The use of this polymer for demanding applications is due to its chemical structure (Figure 3.1) that imparts high glass transition and melting temperatures, around 140 and 340°C respectively (variations depend on the grades), high mechanical properties, which are maintained also at high temperature, and good chemical and thermal degradation resistance. In particular Aryl groups provide modulus, thermal stability, and flame retardance. Ether linkages provide toughness and ductility. Ketones provide long term thermal oxidative resistance. Due to its biocompatibility PEEK is also used
for medical implants. In this thesis work, all studies and experiments were performed on PEEK films having a thickness of either 125 µm or 6 µm.

\[
\begin{align*}
\text{F} & \quad \text{Cl} \\
\text{C} & \quad \text{C} \\
\text{F} & \quad \text{F}
\end{align*}
\]

Figure 3.2 Generic chemical structure of HALAR® ECTFE.

HALAR® ECTFE (ethylene chlorotrifluoroethylene) a semi-crystalline and melt-processable fluoropolymer obtained by copolymerization of ethylene and chlorotrifluoroethylene. Its schematic chemical formula is reported in Figure 3.2 and the \( \frac{n}{m} \) ratio is usually equal or very close to unity. As the chemical formula suggests, it is similar to ETFE (ethylene fluoroethylene), but shows some advantages in terms of fire resistance, surface smoothness and permeation resistance to small molecules. Another key property of this polymer is the elevated optical transparency, while good mechanical properties are given by strong inter-chain interactions due to hydrogen bonding. Despite being a fluoropolymer fluoro-carbon HALAR® ECTFE is a true thermoplastic that can be handled by conventional techniques as extrusion, blow moulding etc. If compared to PVDF, ECTFE is also characterized by higher thermal rating and chemical resistance. Its glass transition and melting points are usually 85° and 242°C respectively. Due to its properties Halar® ECTFE is widely used in the chemical processing industry, the high purity semiconductor market, the wire and cable market, the pharmaceutical industry, films and a variety of other demanding filtration and corrosion protection applications. In this thesis work, all studies and experiments were performed on ECTFE films having a thickness of either 125 µm or 50 µm.

\[
\begin{align*}
\text{F} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{F} & \quad \text{H}
\end{align*}
\]

(a)

\[
\begin{align*}
\text{F} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{F} & \quad \text{H}
\end{align*}
\]

(b)

\[
\begin{align*}
\text{F} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{F} & \quad \text{H}
\end{align*}
\]

(c)

Figure 3.3 Generic chemical structure of SOLEF® PVDF homopolymer (a), copolymer with HFP (b) and copolymer with CTFE (c).

SOLEF® PVDF (polyvinylidene fluoride) is a fluorinated semi-crystalline thermoplastic which is obtained by polymerizing VDF (vinylidene fluoride). As shown in Figure 3.3, besides VDF homopolymers, also copolymers of VDF can be produced with HFP (hexafluoropropene) and with CTFE (chlorotrifluoroethylene). Due to its chemical structure, PVDF has the best mechanical properties among all fluoropolymers, is characterized by excellent permeation resistance to small molecules and good chemical and weathering resistance. As ECTFE, it can be processed using most of the standard extrusion and moulding methods. Copolymers show some advantages with respect to the homopolymer, in particular copolymerization with CTFE or HFP allows improving the cold temperature thermomechanical properties of the polymer. PVDF glass transition temperature is -40° while its melting temperature ranges between 140° and 175°C depending on molecular weight and degree of copolymerization. PVDF is extensively used in the general chemical processing industry, the high purity semiconductor market and the wire and cable industry. This polymer is also finding space
in new applications as Li-ion batteries, Oil & Gas industry, automotive and building industry. In this thesis work, studies and experiments were performed on two different PVDF grades in two different forms:

- Solef® 80 000 Expanded PVDF: foamed samples.
- Solef® 60512: VDF-CTFE copolymer in the form of 300 μm thick moulded plaques

### 3.1 Plasma treatment and metallization

Independently on the final application, much effort was devoted to the optimization of plasma treatment and electrochemical metallization parameters. Plasma processing conditions, in particular, needed to be tailored to the chemical nature of the polymer to allow homogeneous electrochemical metallization with good adhesion. The effect of plasma treatment on different polymeric materials was therefore studied by contact angle, XPS, SEM and AFM to determine the entity of morphological and chemical modifications. Moreover direct validation of the plasma treatment conditions was performed determining the quality of metallic layers deposited by electroless process. Consequently, depending on the application, the properties required for the metallic layer are different, therefore, after studying the nucleation and growth mechanisms, different metals and thicknesses were considered. Morphology, deposition rate and microstructure of the metallic layers were studied by SEM and XRD, while adhesion by cross-cut test and bending.

#### 3.1.1 Plasma treatment of polymers

As thoroughly explained in the literature review, atmospheric pressure plasma treatment is a versatile process that is capable of modifying the surface of several polymeric materials to allow electroless metallization. To have sufficient adsorption of palladium ions, which act as catalysts for the electroless process, the plasma parameters need to be optimized. Moreover, the chemical modification induced by plasma depends on the composition of the polymer, therefore an optimization process is needed for each polymeric material. Two distinct technical solutions, both operating at atmospheric pressure, were adopted depending on the geometry of the polymeric sample: a roll-to-roll open-air dielectric barrier discharge (DBD) plasma was used to treat films and plaques with thickness lower than 300μm, while an open-air plasma jet was used to treat tri-dimensional samples.

#### 3.1.1.1 Dielectric barrier discharge (DBD)

Films and thin plaques were treated by means of a roll-to-roll dielectric barrier discharge plasma equipment operating in open air. This machine is equipped with a water cooled AC generator whose characteristics are reported in Table 3.1. The discharge gases are fed at the cathode, which is composed of three aluminium plaques coated with a dielectric and positioned at a distance of 350μm from the cylindrical grounded electrode. The grounded electrode is water cooled and is free to spin, to allow the polymeric film to run in the gap between electrodes. The machine can be operated both in pressure control and in flow control: in the first case, the feed pressure of the discharge gas can be modulated by means of a pressure gauge; in the second case three ball-float flowmeters are available to modulate the flow of one or more discharge gases. The winding roll is actuated by an electric motor that allows adjusting the dragging speed of the polymeric film.
Despite the cathode is composed by multiple electrodes (Table 3.1), for sake of simplicity the discharge area is considered to be equal to the width times the circumferential length of the portion of the cylindrical electrode opposed to the cathode. Being the width of the cathode and counter electrodes 65 cm and the discharge length 25 cm, the discharge area is considered to be 1625 cm².

Different discharge gases were used, namely N₂, N₂/H₂ and He, whose flux was controlled by means of flowmeters. Combination of gases was also performed, mainly involving He and either of the others. To have an idea of the intensity of plasma treatment on the polymeric samples, the equivalent corona dose, \( D \), was also calculated as follows:

\[
D = \frac{P}{v \cdot w \cdot n} \left[ \frac{W}{m} \right]
\]

(3.1)

Where \( P \) is the discharge power, as read from the control panel of the machine, \( v \) is the dragging speed of the film in m/min, \( w \) the width of the two electrodes (0.65 m) and \( n \) the number of passes.

This equipment was mainly used to treat 125 µm and 6 µm thick films of KETASPIRE® PEEK (KT-820) and 50 µm and 125 µm thick films of HALAR® ECTFE (HALAR® 350LC), all supplied by Solvay Specialty Polymers. During experimental activity, plasma parameters were varied in order to determine the optimal treatment conditions on these polymeric materials to have homogeneous and adherent metallic coatings. Due to the high number of tests performed, to avoid generating confusion in the reader, information regarding the plasma treatment conditions are reported only for some significant samples. Conditions are summarized in two tables, which are referred to ECTFE (Table 3.2) and PEEK (Table 3.3) respectively.
Table 3.2 Summarizing table reporting significant plasma treatment conditions on HALAR® ECTFE.

<table>
<thead>
<tr>
<th>Plasma ID</th>
<th>Gas 1</th>
<th>Flow 1 (nL/min)</th>
<th>Gas 2</th>
<th>Flow 2 (nL/min)</th>
<th>Power (W)</th>
<th>Dragging speed (m/min)</th>
<th>Corona dose (Wmin/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>N₂</td>
<td>0.5</td>
<td>He</td>
<td>3.5</td>
<td>1500</td>
<td>2</td>
<td>1154</td>
</tr>
<tr>
<td>H2</td>
<td>N₂</td>
<td>0.5</td>
<td>He</td>
<td>3.5</td>
<td>3000</td>
<td>2</td>
<td>2308</td>
</tr>
<tr>
<td>H3</td>
<td>N₂</td>
<td>1</td>
<td>He</td>
<td>7</td>
<td>1000</td>
<td>2</td>
<td>769</td>
</tr>
<tr>
<td>H4</td>
<td>N₂</td>
<td>1</td>
<td>He</td>
<td>7</td>
<td>1500</td>
<td>2</td>
<td>1154</td>
</tr>
<tr>
<td>H5</td>
<td>N₂</td>
<td>1</td>
<td>He</td>
<td>7</td>
<td>2000</td>
<td>2</td>
<td>1538</td>
</tr>
<tr>
<td>H6</td>
<td>N₂</td>
<td>1</td>
<td>He</td>
<td>7</td>
<td>2500</td>
<td>2</td>
<td>1923</td>
</tr>
<tr>
<td>H7</td>
<td>N₂</td>
<td>1</td>
<td>He</td>
<td>7</td>
<td>3000</td>
<td>2</td>
<td>2308</td>
</tr>
<tr>
<td>H8</td>
<td>N₂</td>
<td>1</td>
<td>He</td>
<td>7</td>
<td>3500</td>
<td>2</td>
<td>2692</td>
</tr>
<tr>
<td>H9</td>
<td>N₂</td>
<td>1</td>
<td>He</td>
<td>7</td>
<td>4000</td>
<td>2</td>
<td>3076</td>
</tr>
<tr>
<td>H10</td>
<td>N₂</td>
<td>2</td>
<td>He</td>
<td>7</td>
<td>1500</td>
<td>2</td>
<td>1154</td>
</tr>
<tr>
<td>H11</td>
<td>N₂</td>
<td>2</td>
<td>He</td>
<td>7</td>
<td>2500</td>
<td>2</td>
<td>1923</td>
</tr>
<tr>
<td>H12</td>
<td>N₂</td>
<td>5</td>
<td>He</td>
<td>2</td>
<td>2000</td>
<td>4.5</td>
<td>684</td>
</tr>
<tr>
<td>H13</td>
<td>N₂</td>
<td>5</td>
<td>He</td>
<td>2</td>
<td>3000</td>
<td>3</td>
<td>1538</td>
</tr>
<tr>
<td>H14</td>
<td>N₂</td>
<td>10</td>
<td>He</td>
<td>2</td>
<td>3000</td>
<td>4.5</td>
<td>1026</td>
</tr>
<tr>
<td>H15</td>
<td>N₂</td>
<td>10</td>
<td>He</td>
<td>2</td>
<td>2000</td>
<td>3</td>
<td>1026</td>
</tr>
<tr>
<td>H16</td>
<td>N₂</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>2000</td>
<td>3</td>
<td>1026</td>
</tr>
<tr>
<td>H17</td>
<td>N₂</td>
<td>1.5 Bar (pressure)</td>
<td>-</td>
<td>-</td>
<td>3000</td>
<td>4.5</td>
<td>1026</td>
</tr>
<tr>
<td>H18</td>
<td>N₂/H₂</td>
<td>2</td>
<td>He</td>
<td>7</td>
<td>2500</td>
<td>2</td>
<td>1923</td>
</tr>
</tbody>
</table>

Prior to plasma treatment, polymeric films were thoroughly cleaned on both sides with a cloth soaked with isopropyl-alcohol (IPA), in order to remove contaminants, and dried with a gentle air blow. The plasma discharge was allowed to reach stationary conditions, in terms of voltage and frequency, before starting the film winding mechanism, so that the treatment conditions were homogeneous on
the whole length of the polymeric film. To be sure of the significance of the samples, the initial and final portions (approximately 30cm) of the films that underwent plasma treatment were always discarded. Once collected on the winding roll, the films were handled with care in order to avoid contaminations and used for characterization or metallization tests. Once the best plasma treatment condition for the specific polymer was defined, it was applied to all the samples, to perform characterizations and metallization.

### 3.1.1.2 Plasma Jet

Tri-dimensional objects, cannot be treated by means of the roll-to-roll DBD equipment described above; therefore an Openair® plasma jet equipment from Plasmatreat was used for the plasma pre-treatment of samples different from films. The instrument is equipped with a FG5001 generator and an RD1004 rotating plasma torch. The operating parameters of the generator are reported in Table 3.4, while the nozzle is characterized by a rotation frequency of 2600 min⁻¹. Feedstock gases were purified by means of filters, in order to remove any traces of dust, moisture and oil. The feedstock gas pressure was modulated by means of a pressure gauge: the pressure could be different at the inlet of the gauge (depending on the residual pressure of cylinders) but it was reduced to 4 Bar at the outlet so that the plasma torch was fed at 1 to 1.5 Bar.

<table>
<thead>
<tr>
<th>Duty cycle (%)</th>
<th>Max power (W)</th>
<th>Frequency (kHz)</th>
<th>Voltage (V)</th>
<th>Signal type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 – 100</td>
<td>1000</td>
<td>18-23</td>
<td>250-300</td>
<td>Square wave</td>
</tr>
</tbody>
</table>

Relative motion of the sample with respect to the plasma source was performed by means of an x-y-z Cartesian robot from AEB robotics, where x motion was executed by the sample holder stage, while the plasma torch was moved in the y-z plane (Figure 3.5). The Cartesian robot allowed to control the relative distance between the sample and the plasma source and to scan precisely the surface. The robot allowed treating samples with maximum x-y-z dimensions respectively equal to 300, 300 and 150mm. The sample-nozzle distance was varied between 7 and 15 mm during experimentation and the maximum translation speed of the robot was limited to 250 mm/s, although the maximum robot speed was 400 mm/s. This limit was selected to avoid inhomogeneity in the plasma treatment, which could be due to the combination of the rotatory motion of the nozzle and the translational motion of torch and sample stage. Studies were performed to determine the optimal pitch among adjacent passes of the torch on flat surfaces; the effect of plasma treatment is dependent on the distance of the surface from the nozzle, therefore also the lateral displacement of the torch among adjacent passes had to be determined to have a homogeneous treatment. The optimal pitch was determined to be 10mm. For complex geometries, the general guideline was found in keeping both the orthogonal distance between nozzle and surface features and pitch length constant. At the same times some optimization was usually necessary to slightly adjust parameters. Even for foams, the dimension of surface roughness is small if compared to the length of the plasma plume; therefore sample-nozzle distance was fixed with respect to the ideal surface. Finally, due to its penetration ability (it is to be kept in mind that plasma treatment was originally ideated and is most importantly applied to the textile industry), plasma treatment was considered to be effective equally on the surface and in the macroscopic pores present on the surface of the samples.
Experimental Procedures

Solvay Specialty Polymers spa confidential information

Figure 3.5 Picture of the plasma torch mounted on the Cartesian robot and of the feedstock gas filtering and units.

This plasma treatment technology was adopted to pre-treat samples consisting in parallelepipeds of foamed PVDF (polyvinylidene fluoride), supplied by Solvay Specialty Polymers under the commercial name of SOLEF® 80000. Due to difficulties in evaluating plasma treatment on the surface of foamed samples, especially considering contact angle measurements and visual inspection of the metallic deposits, some preliminary studies where performed on flat samples of a similar grade of PVDF. SOLEF® 60512 was supplied by Solvay Specialty Polymers, for this purpose, in the form of 300 µm thick moulded plaques. These samples where thoroughly cleaned with a cloth soaked with IPA and carefully dried before performing plasma treatment, while they were fixed to the stage of the Cartesian robot with adhesive kapton tape. Plasma treatment conditions on these samples are reported in Table 3.5.

Table 3.5 Summarizing table reporting significant plasma treatment conditions on SOLEF® PVDF moulded plaques.

<table>
<thead>
<tr>
<th>Plasma ID</th>
<th>Precursor gas</th>
<th>Voltage (V)</th>
<th>Frequency (kHz)</th>
<th>Duty cycle (%)</th>
<th>Scan speed (mm/s)</th>
<th>Passes</th>
<th>Nozzle distance (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>280</td>
<td>21</td>
<td>100</td>
<td>150</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>S2</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>280</td>
<td>21</td>
<td>100</td>
<td>150</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>S3</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>280</td>
<td>21</td>
<td>100</td>
<td>150</td>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td>S4</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>280</td>
<td>21</td>
<td>100</td>
<td>150</td>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td>S5</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>280</td>
<td>21</td>
<td>100</td>
<td>150</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>S6</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>280</td>
<td>21</td>
<td>100</td>
<td>150</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>S7</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>280</td>
<td>21</td>
<td>50</td>
<td>150</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>S8</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>260</td>
<td>20</td>
<td>50</td>
<td>150</td>
<td>2</td>
<td>11</td>
</tr>
</tbody>
</table>

The foamed samples were cut from bigger blocks of expanded polymer avoiding surface contaminations; this allowed skipping the cleaning step that could lead to unwanted impregnation of IPA in the open porosity of the surface. Presence of IPA would have indeed altered the chemistry of the plasma species close to the surface. Foams were held in the desired position by means of a Hoffman clamp, which was, in turn, fixed to the stage.
Table 3.6 Summarizing table reporting significant plasma treatment conditions on 
SOLEF® PVDF foams.

<table>
<thead>
<tr>
<th>Plasma ID</th>
<th>Precursor gas</th>
<th>Voltage (V)</th>
<th>Frequency (kHz)</th>
<th>Duty cycle (%)</th>
<th>Scan speed (mm/s)</th>
<th>Passes</th>
<th>Nozzle distance (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>N₂</td>
<td>270</td>
<td>21</td>
<td>100</td>
<td>200</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>F2</td>
<td>N₂</td>
<td>270</td>
<td>21</td>
<td>100</td>
<td>200</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>F3</td>
<td>N₂/H₂</td>
<td>250</td>
<td>19</td>
<td>75</td>
<td>250</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>F4</td>
<td>N₂/H₂</td>
<td>250</td>
<td>19</td>
<td>75</td>
<td>250</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>F5</td>
<td>N₂/H₂</td>
<td>280</td>
<td>21</td>
<td>100</td>
<td>250</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>F6</td>
<td>N₂/H₂</td>
<td>280</td>
<td>21</td>
<td>50</td>
<td>250</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>F7</td>
<td>N₂/H₂</td>
<td>270</td>
<td>21</td>
<td>100</td>
<td>150</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>F8</td>
<td>N₂/H₂</td>
<td>270</td>
<td>21</td>
<td>100</td>
<td>150</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>F9</td>
<td>N₂/H₂</td>
<td>270</td>
<td>21</td>
<td>100</td>
<td>150</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>F10</td>
<td>N₂/H₂</td>
<td>270</td>
<td>21</td>
<td>100</td>
<td>200</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>F11</td>
<td>N₂/H₂</td>
<td>270</td>
<td>21</td>
<td>100</td>
<td>250</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>F12</td>
<td>N₂/H₂</td>
<td>270</td>
<td>21</td>
<td>100</td>
<td>100</td>
<td>2</td>
<td>12</td>
</tr>
</tbody>
</table>

The first tests were executed treating only one face of the sample; when a plasma condition appeared to be promising it was applied to the whole surface of the samples (Table 3.6). The dimension of the foamed samples is reported in Table 3.7.

Table 3.7 Dimensions of the PVDF foam samples.

<table>
<thead>
<tr>
<th>Geometry ID</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>76</td>
<td>76</td>
<td>8</td>
</tr>
<tr>
<td>B</td>
<td>76</td>
<td>76</td>
<td>15</td>
</tr>
<tr>
<td>C</td>
<td>76</td>
<td>76</td>
<td>30</td>
</tr>
</tbody>
</table>

As for roll-to-roll DBD, once the best plasma treatment condition was defined, it was applied to all the samples used for metallization and characterization, independently on their geometry.

3.1.2 Characterization of pristine and plasma treated samples

Plasma treated samples were characterized and compared to the pristine samples to determine the influence of different experimental conditions on morphology, chemistry and wettability. Some characterizations reported here were performed on all or most of the sample produced during experimentation, while others only on selected specimens.

3.1.2.1 Contact angle measurements

Contact angle measurements were performed as first step of characterization, to determine the change in wettability imparted by plasma treatment. First of all, measurements were performed on pristine samples of KETASPIRE® KT-820 PEEK, HALAR® 500LC ECTFE and SOLEF® 60512 PVDF, to have a reference value for the materials before plasma treatment.
Figure 3.6 Examples of snapshots (acquired with DSA 25) of drops poured on substrates with different wettability.

Measurements were performed with Drop Shape Analyser DSA25 by Krüss (examples of drop geometries are shown in Figure 3.6). This goniometer is equipped with a dosing system comprising two syringes, therefore allowing simple measurements with two different liquids. The dosing system is automated and allows pouring precise drop volumes at controlled flow rates, while the sample stage needs to be manually actuated. All measurements were performed at room temperature and environmental pressure using two different liquids to determine the surface tension of the samples. Sessile contact angle was measured in static mode with different drop volumes depending on the liquid: drop volume of 6 µl was used for doubly deionized water while 1 µl for diiodomethane (diiodomethane 99% supplied by Alfa Aesar). Pristine samples were cleaned with water and subsequently IPA in prior to the measurement, in order to remove any traces of dirt; careful drying was assured afterwards to avoid contaminations of the surface by water and IPA. Treated samples were characterized within 5 minutes from the plasma treatment avoiding any form of contamination and contact with external bodies. Surface energy of the samples was calculated using the integrated software of the instrument; among the different methods proposed in the software the so-called extended Fowkes method was selected, which coincides with the Owens, Wendt, Rabel und Kaelble method. For each sample, the contact angle was measured at least on four drops of water and four drops of diiodomethane, randomly distributed on the treated surface. If the standard deviation among the four drops of each liquid was smaller than 2°, the measurement was considered successful and acceptable. Differently, if the standard deviation among the contact angles of either liquid was found to be greater than 2°, the measurement was repeated on a new sample.

Ageing studies with contact angle

Ageing studies were performed on films of KETASPIRE® KT-820 PEEK, SOLEF® 60512 PVDF and HALAR® 500LC ECTFE, to determine amount and mechanisms of hydrophobic recovery in time. Two series of ageing studies were performed, the first to determine if the ageing process is either chemical or physical, the second to determine exclusively the effect of temperature. The plasma conditions giving the best results in terms of metallization were selected for both materials; these do not necessarily coincide with the conditions giving the highest increase in surface energy. Both series of ageing studies were performed on PEEK and ECTFE, while only the first on PVDF, with the contact angle measurement procedure reported above. In order to check reproducibility, the measurement was always performed on two samples at any ageing time. All samples were cut from a bigger piece of polymer film, treated by means of the DBD equipment, and stored in the desired condition within 5 minutes. In the first series of ageing studies, a comparison was performed among samples stored at room temperature and pressure, at room temperature under vacuum and at low temperature (-18°C) and pressure. A fourth condition was considered with PEEK, i.e. low temperature and pressure, since the first ageing test was performed on this material. Once proofed that temperature was the main
parameter affecting ageing, on ECTFE and PVDF only the three abovementioned conditions were studied. Storing conditions for the second series of ageing studies are reported in Table 3.8. All samples were wrapped in clean aluminium foil and, for the ones stored at low pressure, the vacuum was applied by means of a commercial kitchen vacuum sealing machine.

### Table 3.8 Summary of ageing conditions for PEEK and ECTFE, where F is Freezer, R is refrigerator, C is Cryostat, AC is Air Conditioning and CO is Convection Oven.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK</td>
<td>4 15 23 40 55 80 120</td>
</tr>
<tr>
<td>ECTFE</td>
<td>4 15 22 40 55 70 80</td>
</tr>
</tbody>
</table>

#### 3.1.2.2 Chemical modification by XPS

X-ray photoelectron spectroscopy was performed both on pristine and on plasma treated samples of KETASPIRE® KT-820 PEEK, HALAR® 500LC ECTFE and SOLEF® 60512 PVDF. Measures were performed, for each plasma treated polymer, within 24h from the treatment, avoiding any surface contamination. Samples were placed inside polymeric petri dishes and sealed using a vacuum sealer. For comparison reasons, the plasma treatment conditions adopted for PEEK and ECTFE are the same as for the ageing studies. Similarly, the ones giving the best metallization conditions were selected for PVDF. X-ray photoelectron spectroscopy measurements were performed using a Kratos Axis DLD ultra. Survey spectra were acquired using a step of 0.5eV, 1 s integration time and pass energy of 160eV. Core lines were recorded using a 0.05 eV step, 1 s integration time and 40 eV of pass energy. This allows obtaining an energetic resolution of about 0.3 eV. Peak fitting was performed imposing linear subtraction baseline and Gaussian components. Quantification was performed using sensitivity factors supplied by the instrument manufacturer. Blank samples were cleaned before the analyses, following the same procedure described for plasma treatment. Treated samples were stored inside sealed petri dishes to avoid environmental contamination and surface alteration during handling.

#### 3.1.2.3 Morphological analysis by SEM, AFM and optical microscopy

Scanning electron microscopy, atomic force microscopy and optical microscopy were used in different combinations to determine the effect of plasma treatment on the surface morphology of the different polymers. Polymeric films, i.e. PEEK and ECTFE, were characterized by means of SEM and AFM, while PVDF foams were characterized by means of SEM and optical microscopy.

AFM measurements were performed on different areas, ranging from 4 µm² to 250 µm², using a NT-MDT Solver Pro instrument in tapping mode. Scanning was performed at first on wide areas and afterwards on smaller and smaller portions of the original surface to detect morphological details at different magnifications. All measurements were performed in air under environmental conditions, avoiding the presence of vibrations by means of a suspended stage. Comparisons were performed between the pristine polymeric films and the samples treated in the selected plasma conditions. Pristine films were cleaned with water and afterwards with IPA to remove surface contaminations, while plasma treated samples were handled avoiding contaminations and any form of surface contact with third bodies. In both cases, after placing of the sample on the stage, eventual presence of particulates or dust was removed with a gentle blow of dry nitrogen.

Optical microscopy was performed on foamed samples at magnification levels ranging from 6.3 x to 20 x by means of a Leica M60 stereomicroscope in reflected light mode.
Scanning electron microscopy was performed both on polymeric films and on foams, before and after plasma treatment, with a Zeiss Leo Supra 35 field emission microscope. Due to the insulating nature of polymers, all samples were coated with a thin metallic layer before being analysed, which assures electrical conductivity to the sample, avoiding charge accumulation. Depending on the availability, either 7nm thick Ir layers or 12nm thick Cr layers were deposited by means of a high resolution sputter coater (Cressington 208HR) operating at 0.1 torr. For PEEK and ECTFE, morphological surface analysis was executed only on samples treated with the plasma conditions that were found to be the best for metallization. On the other end, samples produced with different plasma conditions were tested in the case of PVDF foams, to assess the effect of the treatment conditions on the alveolar morphology of the foamed polymer.

3.1.3 Electrochemical metallization of polymers

After plasma treatment, metallization test were executed to assess the effectiveness of the chemical modification with respect to palladium adsorption. In this framework a first distinction can be done between electroless and electrolytic deposition, further distinctions can be based on the metal that is deposited with the electrochemical process.

3.1.3.1 Electroless deposition of Copper and Silver

Electroless copper metallization, and visual observation of its quality, were used as direct evaluation of plasma treatment for the adsorption of palladium ions in the activation solution. Copper layers were deposited by means of commercial plating baths from Atotech. Table 3. reports time and temperature conditions adopted during experimentation using the Printoganth PV line. The Sn-based pre-dip bath was abandoned shortly after starting experimentation: it was proofed, according to the literature, that it use was superfluous when activating properly the polymer surface by plasma.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Cleaner</th>
<th>R</th>
<th>Pre-dip</th>
<th>Activator</th>
<th>R</th>
<th>Reducer</th>
<th>R</th>
<th>Electroless</th>
<th>FR</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>NH₃ based</td>
<td>25</td>
<td>40</td>
<td>Pd based</td>
<td>30</td>
<td>1</td>
<td>4</td>
<td>NaBH₄ based</td>
<td>1-30</td>
</tr>
<tr>
<td>Time (min)</td>
<td>Sn based</td>
<td>1</td>
<td>3</td>
<td>HCHO based</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Also the use of the cleaner solution was abandoned together with the pre-dip solution since no need to clean the surface was present, thanks to the careful handling procedures adopted for plasma treated samples. When required, thorough rinsing was performed gently squirting deionized water on the surface of the sample by means of a wash bottle. Different experimental setups were adopted depending on sample geometry and on the surface coverage required. Three main setups have been adopted during experimentation, depending on the requirements:

- Small films: especially for the first tests, i.e. during validation of plasma treatment conditions, small samples where cut from the treated films. Depending on their dimension, which could range from 10 to 50 cm², beakers of the appropriate capacity were filled with a suitable volume of the different solutions. Attention was paid to assure the solution to operate in the recommended loading range (around 3 dm²/L). Solutions were stirred by means of heated magnetic stirrers and temperature was controlled by means of Vertex thermocouples. Since metallization needed to be performed only on one surface, samples were fixed on 1.5 mm thick PTFE plates with adhesive kapton tape. Attention needed to be paid to avoid solution
infiltration between the sample and the PTFE plate, which could lead to solution drag-in and contamination. Once carefully fixed, the samples were dipped vertically in the electroless line solutions, according to the sequence reported in Table 3. Slightly different sample fixing procedure was adopted when preparing samples for experiments on circuit breakers. In this case a portion of the back side of the sample needed to be coated with electrical continuity to the front side. For this reason such samples were plasma treated on both sides and also a portion of the back side was exposed to the solutions as shown in Figure 3.7.

![Figure 3.7](image)

**Figure 3.7** Schematic representation of (a) a generic sample mounted on a PTFE plate and (b) front and back views of a sample for the production of circuit breakers

- A4 sized films: once the optimal plasma conditions were defined, bigger portions of polymeric films were metallized using a simple plating line, specifically designed and build for the metallization of A4 sized (roughly 21x30 cm) films. This metallization line is composed of (Figure 3.8):
  - Seven PVC tanks (capacity 1L) for the cleaning, pre-dip, activation and reduction solutions with the respective rinsing steps.
  - One PVC tank, internally coated with PTFE, (capacity 11L) for the electroless deposition solution. Solution agitation is obtained by means of a mechanical stirrer.

The temperature of each solution was controlled by means of PTFE coated immersion heaters, equipped with a thermocouple and connected to control electronics. Similarly to Figure 3.7 (a), the polymeric films were fixed on a 3mm thick PTFE plate (22x35cm) that could be dipped and secured in all eight tanks, thanks to the presence of suitable grooves in the lateral walls of the tanks themselves. Making exception for the different geometry of the tanks, the plating procedure was the same as for small regular films, reported above.
Foams: Due to their low apparent density (as low as 60g/L) and the need to coat the whole surface, a specific setup was developed for the metallization of foamed PVDF. Square PTFE Frames, 2 cm larger and 2 cm taller than the polymeric foams were produced, having through holes in the four corners and a removable handle. After plasma treatment, a thin copper wire (about 200µm of diameter) was passed, with the help of a needle, through the foam in the proximity of each of the four corners of the square surface. The four copper wires were therefore secured to the four holes in the frame so that the sample was tightly placed at the centre of the frame without touching it (Figure 3.9). The electroless deposition solutions were contained in 3L beakers; their agitation and temperature were controlled as described above for small films. Despite the presence of the frame, the buoyancy force acting on the samples was relevant, therefore the handle of the frame was secured to a stand by means of suitable clamps. This setup assured the foam to be immersed and firm in the solution even under the stirring conditions required during electroless deposition to avoid gas bubbles to be trapped in surface porosity. This setup was not adopted for the first feasibility tests, when only one surface of the foam was plasma treated. In this last case the sample was manually dipped in the solutions.
Besides the differences described above, which depended mainly on the dimensions and geometry of the polymeric samples, the main parameter that was varied among the samples that were prepared is the deposition time that ranged between 1 min for small samples of film and 30 min for some of the foams.

Electroless Ag deposition was also performed, with internally developed solutions, exclusively on HALAR® 350LC ECTFE. The solutions prepared for this purpose are:

- **Activation:**
  - Deionized H₂O: 96 ml
  - SnCl₂ (Merck Millipore): 5 g
  - HCl 35% (Sigma-Aldrich): 4 ml
- **Deposition:**
  - Deionized H₂O: 100 ml
  - AgNO₃ (99% Sigma-Aldrich): 1.67 g
  - NH₄OH (28-30% Sigma-Aldrich): 23.5 ml
  - NaOH 20%wt solution (98% Sigma-Aldrich): 4.7 ml
- **Reduction:**
  - Deionized H₂O: 10 ml
  - C₆H₁₂O₆ (99.5% Sigma-Aldrich): 0.56 g

The internally developed deposition process requires the sample to be immersed in the activation solution, without stirring, for 5 minutes at room temperature. Once removed from the activation bath the sample is rinsed gently with water and finally it is immersed in the deposition solution. This bath is maintained around 10°C to minimize spontaneous silver precipitation; 10 s after the immersion of the sample, 140 µl of the reduction solution are added every 10 ml of deposition bath. The solution is manually oscillated until the sample is removed. Besides this process, some trials were performed with the commercial activation solutions used for copper deposition, namely: one series of tests using only the commercial activation solutions and a last set of experiments combining the two activation processes. The sequence of the three series of experiments is reported in Table 3.9. It is to be noted that the commercial activation baths were used in the same conditions as for copper deposition (see Table 3.) and the internally developed solutions were used as abovementioned. The activation solutions, both internally developed and commercial, were contained inside 200 ml beakers where the sample was vertically immersed. The deposition process, on the other end, was performed positioning the activated sample on the bottom of a glass petri dish, to minimize the utilization of solution. During deposition silver precipitation occurs, therefore each metallization needs a freshly made solution; 15
ml of deposition solution were used to coat one face of each rectangular polymeric sample (approximately 3 cm wide and 4 cm long).

Table 3.9 Sequences used for the three series of Ag deposition tests. Where IA is the internal activation, Ag is silver deposition, CA and CR commercial activation and reduction respectively.

<table>
<thead>
<tr>
<th>Series</th>
<th>Step 1</th>
<th>Step 2</th>
<th>Step 3</th>
<th>Step 4</th>
<th>Step 5</th>
<th>Step 6</th>
<th>Step 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series I</td>
<td>IA</td>
<td>Rinse</td>
<td>Ag</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Series II</td>
<td>CA</td>
<td>Rinse</td>
<td>CR</td>
<td>Rinse</td>
<td>Ag</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Series III</td>
<td>IA</td>
<td>Rinse</td>
<td>CA</td>
<td>Rinse</td>
<td>CR</td>
<td>Rinse</td>
<td>Ag</td>
</tr>
</tbody>
</table>

Ag deposition usually started after an induction time of approximately 2 minutes; total deposition times ranged between five and twenty minutes depending on the experimental conditions adopted.

Finally some samples were produced depositing both silver and copper by electroless process. In particular, after coating plasma treated HALAR® 350LC ECTFE with silver, using the sequence described for Series II, the sample was immersed in the commercial electroless copped bath for a time ranging between one and five minutes.

### 3.1.3.2 Electrodeposition of copper

Electrodeposition was performed, when thicker metallic layers were needed, on samples that had already been metallized by electroless deposition with a sufficiently conductive layer. Copper electrolytic deposition was performed using a commercial acidic bath supplied by Tecnochimica. This plating bath was operated at room temperature, under gentle stirring. The recommended operative current density was 15mA/cm² and a soluble Cu (doped with S to improve solubility) ingot was used as anode. The experimental setup depended on the dimension and geometry of the samples to be plated. Namely:

- Small films: in this category are included all the samples smaller than 50 cm², due to the dimension of the copper counter electrode, even for small samples, a 3 L beaker was filled with the amount of solution necessary to immerse the whole sample to be electroplated. A 5 L beaker was used for samples that could not fit in the smaller container. For this kind of samples only a portion of the surface, slightly smaller than the electroless copper layer, was coated by electrodeposition. Sample preparation and electrical contacts are performed, so that the sample results as reported in Figure 3.10. A frame, partially overlapping on the electroless copper, was formed with adhesive copper tape and contacted with the insulated copper wire, which is connected with the negative pole of the generator. A further kapton tape frame was afterwards applied to the sample, both to mask the adhesive copper tape and to fix the sample to a 1.5 mm thick PTFE plate, used as support.
• Large films: this category included all the samples larger than 50cm² up to the size of an A4 sheet. The setup used for this kind of samples, internally designed and produced, was originally ideated for A4 sized films obtained with the metallization line reported above, but afterwards adopted also for smaller samples. The sample preparation procedure is qualitatively identical to the one described for small films and reported in Figure 3.10; the only difference is the use of the larger PTFE support shown in Figure 3.8. The deposition tank is reported in Figure 3.11 (a). Mechanical agitation could be performed by means of one or two motors placed laterally with respect to the sample and the counter electrode. Even though this copper electrodeposition bath was used at room temperature, the use of immersion heaters was possible.

• PVDF Foams: due to the different geometry and the need of metallizing the whole surface, a slightly different experimental setup was used for these samples. A 5 L beaker was adopted to contain the solution, as for small films, but the main difference comes from the need of coating the whole surface of the sample. Electrical contacts were established ad depicted in Figure 3.11 (b): the sample is placed at the centre of a PTFE frame and the insulation layer was removed from some portions of the conductive wire to expose its strands. The peeled wire was therefore passed in the holes of the frame to establish the electrical contact and hold the sample in position. The two ends of the wire where therefore short-circuited and connected to the negative pole of the potentiostat/galvanostat. The sample, mounted on the frame, was therefore immersed in the plating solution opposed to the soluble anode. Each face of the sample was held facing the anode for half of the total electrodeposition time, in order to favour homogeneous metal thickness distribution on the surface.

**Figure 3.10** Schematic representation of the sample preparation procedure for electrodeposition on films. (a) the sample is placed on the PTFE support, (b) a frame is formed with copper tape, connected with the insulated wire and (c) the sample is masked with kapton.
To assure that the electroless metallic layer was free from surface oxides, which would have negatively affected electrodeposition, all the samples were either dipped in diluted sulphuric acid (2 %wt) or immersed in the acidic electrodeposition bath for approximately 5 s before starting plating.

3.1.4 Characterization of metallized polymers

Once the quality of metallization passed visual inspection, samples were characterized to gather information concerning the polymer-metal adhesion (bending and cross cut tests), the microstructure of the metallic layer (XRD) and the nucleation and growth processes (SEM).

3.1.4.1 Evaluation of adhesion

Although not properly designed for metallic deposits, adhesion was tested with the cross-cut test in compliance with the D3359 ASTM norm; this is due to the low thickness of the metallic deposit usually adopted during this work. This test is performed as follows:

- The surface to be tested is clean and dry
- With a dedicated tool, equipped with six sharp edges, two orthogonal cuts are performed on the metallic layer. Attention must be paid to reach the polymer underneath. With this operation a portion of the metallic deposit is cut to form twenty-five squares.
- An adhesive tape, with certified adhesion force, is placed at the intersection of the cuts, oriented in the same direction as one of the cuts (therefore orthogonal to the other). It is adhered accurately to the coating with one finger, leaving one end free for pulling.
- Once the tape has homogeneously adhered to the test zone, within one minute the tape is pulled steadily from the free end, forming an angle as close as possible to 180° between the adhesive layer and the coating.

Finally the amount of coating removed is determined by visual inspection and the adhesion class is determined according to Table 3.10. Where 5B is the highest adhesion level and 0B the lowest.
Table 3.10 Classification of adhesion level according to ASTM D3359.

<table>
<thead>
<tr>
<th>Classification</th>
<th>5B</th>
<th>4B</th>
<th>4B</th>
<th>2B</th>
<th>1B</th>
<th>0B</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of area removed</td>
<td>0</td>
<td>&lt;5</td>
<td>5-15</td>
<td>15-35</td>
<td>35-65</td>
<td>&gt;65</td>
</tr>
</tbody>
</table>

Schematic example

To improve the discrimination among different plasma treatment conditions, adhesive tapes with different certified adhesion forces were used. Namely:

- 3M paper masking tape 2214, 19 mm wide, adhesion force on steel 2.4 N/cm
- 3M 69 Glass Cloth Electrical Tape, 19 mm wide, adhesion force on steel 4.4 N/cm
- 3M Scotch Filament Tape 898, 18 mm wide, adhesion force on steel 7.7 N/cm
- 3M Scotch Tape 389, 25 mm wide, adhesion force on steel 9 N/cm

Besides adhesion force also flexibility was considered an important parameter, in this case bending test was performed in compliance with the ISO 1519:2011 standard. This test can be performed with two approaches:

- as a “pass/fail” test, by carrying out the test with a single specified size of mandrel, to assess compliance with a particular requirement;
- By repeating the procedure using successively smaller mandrels to determine the diameter of the first mandrel over which the coating cracks and/or becomes detached from the substrate.

Figure 3.12 Schematic representation of type 1 apparatus used for bending test.
Where 1 is the mandrel and 2 is a stop.

In this case, the test was executed according to the second approach. Since the thickness of the samples was smaller than 0.3 mm, type 1 apparatus was used (Figure 3.12): the apparatus was completely opened, equipped with the mandrel of desired diameter, and the sample was inserted so that it was subsequently bent with the coated side outwards. The apparatus was closed at a steady rate without jerking, over a period of 1 s to 2 s, thus bending the sample through 180° over the mandrel. The sample was finally visually inspected, without being removed from the apparatus, to determine the presence of cracks. Different mandrels were used having diameter of 2 mm, 3 mm, 4 mm, 5 mm, 6 mm, 8 mm, 10 mm, 12 mm, 16 mm, 20 mm and 25 mm.
3.1.4.2 Metal nucleation and growth - SEM

Nucleation and early growth stages of copper and silver during electroless deposition were studied by means of SEM. All analyses were performed with a Zeiss Leo Supra 35 field emission microscope. Partly imaging process, but mainly sample preparation were different depending on the type of sample:

- Nucleation tests: at very low electroless deposition times, some samples did not possess the necessary conductivity to perform imaging, therefore depending on the availability, either 7nm thick Ir layers or 12nm thick Cr layers were deposited by means of a high resolution sputter coater (Cressington 208HR) operating at 0.1 torr. These tests were performed imaging the surface of the samples orthogonally. Samples showing sufficient conductivity where not sputter coated before imaging.

- Growth tests: these tests were performed to determine the deposition rate once a continuous layer of metal was formed on the polymer surface. The samples were cut in nitrogen to minimize plastic deformation at the surface of fracture. Cross sectional imaging was performed after the deposition of about 20 nm thick Cr layers, by means of a high resolution sputter coater (Cressington 208HR) operating at 0.1 torr. This was necessary since the polymer cross-section is not conductive and charge accumulation would otherwise occur.

<table>
<thead>
<tr>
<th>Table 3.11 Summary of experimental conditions used for the generation of samples for nucleation studies with SEM.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>PEEK</td>
</tr>
<tr>
<td>ECTFE</td>
</tr>
<tr>
<td>ECTFE</td>
</tr>
</tbody>
</table>

These studies were performed on HALAR® 350LC ECTFE and KETASPIRE® KT-820 PEEK in different experimental conditions. Information regarding sample production for nucleation tests is reported in Table 3.11. Electroless deposition time equal to zero represents the plasma treated polymer. Growth studies were performed mainly on ECTFE, due to difficulties in sample preparation for PEEK, experimental conditions for the production of specimens are reported in Table 3.12.

<table>
<thead>
<tr>
<th>Table 3.12 Summary of experimental conditions used for the generation of samples for growth rate studies with SEM.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>ECTFE</td>
</tr>
<tr>
<td>ECTFE</td>
</tr>
</tbody>
</table>

It can be noted that only one electroless deposition time (720s) was considered for the evaluation of the thickness of silver on HALAR®. This was because interest was devoted to the determination of the maximum thickness achievable, before silver precipitation in the solution. Deposition rate studies where not performed for electrodeposition, since they were supplied within the technical data sheet of the acidic copper deposition bath. Only one test was performed to verify this information on a sample produced in the conditions reported in Table 3.13.

<table>
<thead>
<tr>
<th>Table 3.13 Experimental conditions used for the production the sample for evaluation of thickness of electrodeposited copper with SEM.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>ECTFE</td>
</tr>
</tbody>
</table>
Finally, indications regarding the crystalline size of the metallic deposits were collected, to be compared with the results obtained from XRD.

### 3.1.4.3 Microstructural analysis by XRD

X-ray diffraction spectroscopy was performed on some samples to determine the crystalline structure and to have indications regarding the crystallite size of the metallic deposits produced in different conditions. Samples were analysed with a Philips Xpert Pro instrument, equipped with a ceramic tube with copper anode having K-Alpha1 wavelength equal to 1.54056 Å and K-Alpha2 wavelength equal to 1.54439 Å. The power supply was set at 40 kV and 40 mA. Continuous scan was performed with the following parameters:

- $2\theta$: comprised between 5° and 80°
- Step size: 0.050°
- Time for each step: 10.00 s
- Scan Speed: 0.005°/s

This analysis was performed only on some samples, namely:

a. One sample of silver coated ECTFE, produced according to series II of Table 3.9, deposition time 720 s
b. One sample as "a" subsequently coated with electroless copper for 180 s
c. One sample of electroless copper coated PEEK, deposition time 180 s

Where all PEEK samples were treated in the P5 condition and all the ECTFE samples in the H5 condition.

The Scherrer method was also applied to double check the crystallite size, obtained by SEM imaging, of some of the metallic coatings. First of all the applicability of this method was verified since all deposits considered were characterized by crystallites smaller than 200 nm. The Scherrer method allows correlating diffraction peak broadening to the dimension of crystallites, once verified that their dimension is smaller than approximately 200 nm. In particular the effect of average grain size ($\tau$) on Bragg peak broadening ($\beta$, in radians) can be expressed as follows:

$$\beta = \frac{\lambda}{\tau \cos \theta} \quad (3.2)$$

Where $\theta$ is the diffraction angle and $\lambda$ the incident radiation wavelength[1].

### 3.2 Application-oriented characterization

Besides fundamental characterizations, which were executed to understand the basics of the plasma treatment and metallization processes, further testing was performed to validate the proof of concept of this technological solution for four different applications.

#### 3.2.1 Solar concentrator mirrors – UV-VIS-IR spectrophotometry

Due to its intrinsic chemical and physical properties, necessary for this application, only HALAR® was used as polymeric substrate. Spectrophotometric measurements were performed using Perkin Elmer Lambda 2 spectrophotometer, both in reflection and transmission modes, with integration sphere; measures were performed using incident radiation on the polymeric side of the samples. Collected
data are relative to the reference sample of Spectralon (from Labsphere, Inc.). The sampling wavelength was varied between 200 nm and 1100 nm.

The analysis was performed on the samples reported in Table 3.14, where internal activation and commercial activation refer to the internally developed activation process for Ag electroless and commercial activation line for Cu electroless (from Atotech) respectively.

Table 3.14 Summary of experimental conditions used to produce samples for spectrophotometric characterization. EL stands for electroless and ED for electrodeposition.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>CM1</th>
<th>CM2</th>
<th>CM3</th>
<th>CM4</th>
<th>CM5</th>
<th>CM6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>EL Cu, 180 s</td>
<td>EL Cu, 180 s</td>
<td>EL Ag 600 s</td>
<td>EL Ag, 720 s</td>
<td>EL Ag, 720 s</td>
<td>EL Ag, 720 s</td>
</tr>
<tr>
<td>Layer 2</td>
<td>-</td>
<td>ED Cu, 600 s</td>
<td>-</td>
<td>-</td>
<td>EL Cu, 60 s</td>
<td>EL Cu, 120 s</td>
</tr>
<tr>
<td>Comments</td>
<td>Commercial activation</td>
<td>Commercial activation</td>
<td>Internal activation</td>
<td>Commercial activation</td>
<td>Commercial activation</td>
<td>Commercial activation</td>
</tr>
</tbody>
</table>

All ECTFE substrates were plasma treated in the H5 condition. It is to be noted that sample CM1 and CM2 were obtained from the same HALAR® film, metallized with the A4 setup. Layer 1 of CM2 is therefore identical to CM1 and electrodeposition was performed in a second moment. Differently, due to the small dimension of samples that could be coated with the electroless Ag process, CM5 and CM6 were produced with two different batches of solution in different experiments, although using the same conditions. Moreover Layer 2 was deposited immediately after rinsing the sample subsequently to electroless Ag deposition.

### 3.2.2 Metallized micro-speaker diaphragms

The effect of a thin metallic layer deposited on polymeric diaphragms was determined in terms of thermal conduction and mechanical properties. The first is measured to show the advantage of a metallized component with respect to a bare film, the second is evaluated to assess the side effects caused by the metallization process. Samples were prepared in the same experimental conditions for both characterizations, i.e. infrared thermography and micro-tensile testing, (Table 3.15):

Table 3.15 Summary of experimental conditions used to produce samples for characterization. EL stands for electroless and ED for electrodeposition.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>MS1</th>
<th>MS2</th>
<th>MS3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>EL Cu, 180 s</td>
<td>EL Cu, 180 s</td>
<td>EL Cu 180 s</td>
</tr>
<tr>
<td>Layer 2</td>
<td>-</td>
<td>ED Cu, 100 s</td>
<td>ED Cu, 160 s</td>
</tr>
</tbody>
</table>

Samples used for both IR thermography and tensile testing were produced starting from a 6 µm thick PEEK film, plasma treated in the P5 condition. Electroless metallization was executed on two A4-sized polymer portions, using the dedicated plating line: one sheet was used for producing specimens for IR-thermography, while the other sheet for generating specimens for micro-tensile testing. Each of the two electroless plated polymer sheets were divided into three equal portions, approximately 9x18 cm in size. MS2 and MS3 samples were obtained electrodepositing copper with the commercial acidic plating solution. Every electrodeposition experiment was performed on half of the individual electroless samples, i.e. on 9x9 cm sized samples (Figure 3.13).
Figure 3.13 Schematic representation of the samples used for characterization. From left to right: bare PEEK film, film after electroless Cu deposition and final samples (after electrodeposition for MS2 and MS3).

3.2.2.1 Infrared thermography

Thermal characterization was performed using a P 640 thermal camera from FLIR, having spectral range 7.5–13 μm. The experimental setup is schematically represented in Figure 3.14 and comprised: a galvanostat/potentiostat EA-PSI 8080-40 from Elektro Automatik, used to impose the selected continuous current to a voice-coil (10 mm outer diameter), which was recovered from a commercial loudspeaker. The current flowing in the circuit was double-checked with a multimeter, U1232A from Agilent Technologies. The solenoid was placed against the polymeric film facing, when present, the metallized surface. The film was tightened using a circular sample holder, 60 mm of diameter. The temperature of the solenoid was verified by means of a thermocouple and the thermal camera was positioned at 350 mm orthogonal to the film surface and on the opposite side with respect to the heat source.

In order to determine the absolute temperature of the sample, emissivity of the metallized polymeric samples was determined, using a Perkin Elmer Lambda 2 spectrophotometer, on the polymeric surface. Two different series of experiments were performed:

- Equilibrium temperature: the solenoid was heated by means of a constant current and imaging was performed once the system reached thermal equilibrium.
- Cooling profile: once the system reached thermal equilibrium the power was switched off and imaging was performed for 60 s to determine the cooling profile of the different samples

For both series of experiments the current flowing in the system was comprised between 130 and 132 mA and in both cases the three metallic deposit thicknesses (MS1, MS2 and MS3) were considered and compared.

### 3.2.2.2 Micro-tensile testing

In order to determine the variation of mechanical properties, induced by the different thickness of copper deposited on PEEK, tensile testing was performed by means of an in-house developed micro-tensile stage (Figure 3.15). The moving grip of the stage, having range of motion of 25 mm, and a displacement resolution of 50 nm, was actuated by a DC gear motor (M112.2DG, Physik Instrumente). The applied load was measured at the fixed grip of the stage by means of a miniature stainless steel load cell (Model 8431, Honeywell). The maximum measurable load was 5 N both in tension and compression, with a resolution of 10 mN. The dead-weight method was adopted to perform calibration of the voltage/force relationship of the load cell. Aluminium was used to fabricate the stand and the mechanical components needed to secure motor and load cell, in order to reduce the overall weight of the system. Elongation was applied with a displacement rate of 1 μm/s. The local failure behaviour was investigated by imaging the sample surface with a stereomicroscope (SZ51, Olympus). Since relevant information is collected in the early stages of deformation, not all samples were tested up to failure.

![Figure 3.15 Photograph of the micro-tensile stage during a test.](image)

Sample preparation, developed to assure reliable and reproducible measurements, was performed according to the following steps:

- A bi-adhesive tape mask was applied on the polymeric side of the samples (Figure 3.16(a)). This subsequently allows handling and securing the thin film on the tensile stage, without altering the measurement zone of the sample.
- Four holes were produced at the round incisions in the mask, by means of a die cutter and a hammer.
- Some portions of the paper protection of the bi-adhesive tape were removed, therefore exposing the adhesive layer.
- Two magnets were placed at the centre line of the mask (Figure 3.16(b)).
- Two parallel cuts were performed with a razor blade, tightened in a suitable holder, and a hammer, using the magnets as guides.
• The magnets were removed and two polymeric masks, each having an half circle of emery-paper that ensures gripping the sample, were placed on the exposed adhesive tape (Figure 3.16(c))

• The perimeter of the mask was cut to free the sample from the rest of the metallized film. Also in this case using a razor blade, tightened in a suitable holder, and a hammer (Figure 3.16(d))

• The sample was mounted and fixed with screws to the grips and the external portion of mask and film were cut using scissors. Attention was paid not to damage the measurement zone.

![Figure 3.16 Sequence of sample preparation stages: (a) bi-adhesive mask is applied on the metallized film, (b) holes are performed (c) polymeric mask are adhered and (d) the sample is cut.](image)

### 3.2.3 Polymer-metal circuit breakers

As for micro-speakers, samples produced in the same experimental conditions were used to perform two different tests. In this case this implied producing temperature-deflection curves and determining the actuation current of the metal-polymer circuit breakers. For this application 125 µm thick KETASPIRE® KT-820 PEEK films were used. Samples were obtained by electroless and electrolytic metallization, performed, after plasma treatment in the condition P5, according to the parameters reported in Table 3.16.

#### Table 3.16 Summary of experimental conditions adopted during electrochemical metallization and free length of the samples used for testing. EL refers to electroless and ED to electrodeposition.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>CB1a</th>
<th>CB1b</th>
<th>CB2a</th>
<th>CB2b</th>
<th>CB3a</th>
<th>CB3b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>EL Cu, 180 s</td>
<td>EL Cu, 180 s</td>
<td>EL Cu, 180 s</td>
<td>EL Cu, 180 s</td>
<td>EL Cu, 180 s</td>
<td>EL Cu, 180 s</td>
</tr>
<tr>
<td>Layer 2</td>
<td>ED Cu, 240 s</td>
<td>ED Cu, 240 s</td>
<td>ED Cu, 360 s</td>
<td>ED Cu, 360 s</td>
<td>ED Cu, 480 s</td>
<td>ED Cu, 480 s</td>
</tr>
<tr>
<td>Free length</td>
<td>20 mm</td>
<td>30 mm</td>
<td>20 mm</td>
<td>30 mm</td>
<td>20 mm</td>
<td>30 mm</td>
</tr>
</tbody>
</table>

Both electroless and electrodeposition were executed in the standard conditions reported above. It can be noticed that for example CB1a and CB1b were obtained in the same conditions: electroless and electrodeposition were indeed performed on 40 x 60 mm sized films, according to Figure 3.7 (b); therefore the samples were cut from this bigger pieces of metallized PEEK, having well defined dimensions, namely (Figure 3.17 (a)):

- Total length: 40 mm
- Width: 3 mm
Experimental Procedures

- Back side metallization length: 4mm

**Figure 3.17** (a) schematic representation of a circuit breaker and (b) photograph of a 30 mm free length sample during one test.

The free length reported in Table 3.16 is referred to the portion of the sample that is free to deflect during testing; therefore it’s equal to the total length minus the grip length. In Figure 3.17 (b) a photograph of a sample is reported having free length equal to 30 mm.

### 3.2.3.1 Determination of actuation current

In order to determine the actuation current of the polymer-metal circuit breakers (also referred to as switches), the experimental setup described in Figure 3.18 was adopted: a simple circuit was formed where the electric power was supplied by means of galvanostat/potentiostat EA-PSI 8080-40 from Elektro Automatik. The current flowing in the circuit was double-checked with a multimeter, U1232A from Agilent Technologies. The circuit breakers were used to close the circuit, having one end fixed by the conductive grip, and the other free to move, and therefore to break the circuit, when the threshold current was overcome. The current was gradually increased to reach the actuation value; therefore the power was shut-down to cool the switch and allow the circuit to close. Afterwards the previous current was applied to verify system actuation.

**Figure 3.18** (a) schematic representation of the experimental setup and (b) close-up photograph of the switch during actuation.

Due to the simple design of the system, the switch sequentially opened and, once cooled, closed the circuit; In order to determine the actuation current for a given geometry, the following requirements needed to be satisfied:

- After applying the selected current, the switch had to be actuated within 10 s
- At least 50 on-off cycles had to be sustained by the switch without shutting down the power and varying the current
- If the power was shut down after each actuation, the switch had to activate at the same current value for at least 50 times.
The switch had to close the circuit after every actuation for at least 50 times.

These requirements were determined to assure reproducibility and reliability for the system. All tests were performed limiting the voltage at 5 V. Both contact and conductive grip were secured tightly using clamps, in order to avoid unwanted relative displacements that would have affected the measurements. The relative distance between contact and grip was set to 26 mm, when testing samples with 30 mm of free length, and to 16 mm when testing sample with 20 mm of free length. The contact length was therefore maintained constant and equal to the back side metallization length for all samples, i.e. 4 mm.

3.2.3.2 Determination of thermal deflection curves

In order to determine the linearity range and the maximum operative temperature of the polymer-metal stripes, thermal deflection curves were determined using a simple experimental apparatus: a common sample holder for cross-sectional images with SEM was carefully glued to a 3 mm thick glass plate. A portion of an adhesive metallic meter was cut and attached to the glass plate, orthogonally to the groove in the sample holder. The sample, i.e. the polymer-metal strip, was tightened using the screws of the sample holder and a small polymeric plaque, so as to distribute homogeneously the load and avoid unwanted deformations (Figure 3.19 (a)). Once the sample was properly secured, the glass plaque was placed inside a glassy Petri dish, containing an inert high boiling liquid, i.e. Galden HT 170 from Solvay Specialty Polymers. The amount of Galden was sufficient to have the sample completely immersed.

The test was therefore performed placing the petri dish on a heater equipped with a thermocouple, which was dipped in the inert liquid, close to the polymer-metal strip. Gradual heating was applied to the system with steps of 10 °C. The deflection value was measured, for each temperature step, after 1 min of stabilization, from room temperature up to 130°C. Alignment marks, which can be noticed on the right hand side of the glass plaque in green (Figure 3.19 (b)), were used to minimize errors in the determination of the deflection value. A pair of marks was indeed produced with a pitch of 5 mm in the same position of both sides of the glass plaque. Aligning the appropriate marks, depending on the position of the free end of the sample, allowed minimizing measurement errors. The deflection was determined by measuring the relative displacement of the free end of the sample, with respect to the initial position at room temperature.
3.2.4 Metallized foams for aerospace – smoke toxicity test

Metallized foams were characterized in order to determine the amount and toxicity of the smoke produced during flaming test. Comparative tests were performed between the pristine and metallized samples. The samples used for this test have the dimensions reported in Table 3.7, namely one set of pristine and two sets of metallized samples were tested for each dimension, i.e. geometry ID A, B and C. Each set was composed by three samples for each dimension, in order to assure reproducibility; therefore a total of 27 samples were tested. The samples were obtained according to the details reported in Table 3.17.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>MFx1</th>
<th>MFx2</th>
<th>MFx3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry ID</td>
<td>A,B,C</td>
<td>A,B,C</td>
<td>A,B,C</td>
</tr>
<tr>
<td>Layer 1</td>
<td>-</td>
<td>EL Cu 15 min</td>
<td>EL Cu 15 min</td>
</tr>
<tr>
<td>Layer 2</td>
<td>-</td>
<td>-</td>
<td>ED Cu 20 min</td>
</tr>
</tbody>
</table>

The main aim of this test was determining the amount of HF in the smoke produced when exposing the sample to a heat source. In detail the test was performed as follows:

- Before starting the test the specimen was wrapped in an aluminum foil for all but the front-facing side. This was performed for two reasons: prevent melting samples to escape from the heat/flame and avoid sticking to the sample holder (Figure 3.20 (a)).
- The wrapped sample was placed in the sample holder, with the free surface outwards. Afterwards the sample holder was placed in the test chamber.
- Two heat sources were present in the test chamber (Figure 3.20 (b) and (c)): a furnace, emitting radiant heat (2.5 W/cm²) to the sample surface and six flames, produced by 3mm cones, oriented in three different directions. Two flames were facing downwards on the lower lip of sample holder, two were perpendicular to the surface and two in between (45°).
- When the test started, the sample was shifted in front of the heat sources, exposing the free surface, and left there for 4 min. After this time the specimen was removed from the heat source.
- During the whole test, smoke evolution was measured by means of an optic instrument inside the chamber.
- After the 4 min of test, the atmosphere inside the testing chamber was pumped and sent to gas detectors, to analyse its composition, specifically the amount of HF.
Figure 3.20 (a) photograph of a sample wrapped in Al foil, (b) picture of the heat sources and (c) schematic representation of the experimental setup.

Bibliography

Chapter 4
Results and Discussion

In order to emphasize the evolution of the research activity, results are organized and divided according to the polymeric material used as substrate for metallization. In this way, for each material, the presentation and discussion of data starts from plasma treatment goes through metallization and arrives to the final application, being supported by the respective characterizations. Therefore results are discussed separately for KETASPIRE® KT-820 PEEK, for HALAR® 350 LC ECTFE and for SOLEF® 60512-80000 PVDF.

4.1 HALAR® 350 LC ECTFE

As abovementioned and according to the structure of the previous chapter, discussion of results is presented according to the conceptual, and chronological, development of research activity. The sections regarding each polymeric material describe first of all plasma treatment and its effect on chemistry, wettability and morphology of the polymer. Subsequently characterization of the metallic layer is presented and, finally, the performances measured for the key properties are discussed, depending on the application.

4.1.1 Plasma treatment

Plasma treatment was performed to introduce nitrogen-bearing functionalities on the surface of the polymeric materials; due to the polar nature of such chemical functionalities, a direct consequence of this process is the increase of the polar component of surface tension, measured by contact angle. In the previous chapter, a list of plasma treatment conditions is reported in Table 3.2, which is representative of the wide number of trials performed. According to the literature, addition of small amounts of H₂ (up to 5%) to N₂ can improve the effect of plasma treatment on partially fluorinated
polymers [64,98]. Forming gas was also used during the plasma treatment of ECTFE, but although giving satisfactory results, it was abandoned since it was more expensive than N₂ alone and didn’t show significant advantages during metallization. This is the reason why only one condition is reported for forming gas, which is the one that gave the best results in terms of metallization. The first test performed to validate a given set of plasma parameters was the measurement of contact angle, immediately after plasma treatment. Before entering in the details, it is of paramount importance to highlight that the results hereby discussed (in this section and in all the following regarding plasma treatment and its effects) are relative to the specific plasma equipment used. It is therefore possible to apply only qualitatively these results to other equipment or experimental apparatuses.

### 4.1.1.1 Contact angle and ageing studies

The initial idea was that higher surface tension, and therefore lower water and diiodomethane contact angles, had to be connected with a higher amount of nitrogen-bearing groups and therefore higher effectiveness of plasma treatment. For this reason, the goal of the first pre-activation studies was to find the plasma condition able to increase as much as possible the surface tension of the polymer.

<table>
<thead>
<tr>
<th>Plasma ID</th>
<th>Contact angle (%)</th>
<th>Surface tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
<td>Diiodomethane</td>
</tr>
<tr>
<td>H1</td>
<td>48</td>
<td>40.5</td>
</tr>
<tr>
<td>H2</td>
<td>49.1</td>
<td>47.6</td>
</tr>
<tr>
<td>H3</td>
<td>61.6</td>
<td>46.1</td>
</tr>
<tr>
<td>H4</td>
<td>54.4</td>
<td>45.5</td>
</tr>
<tr>
<td>H5</td>
<td>52.1</td>
<td>45.4</td>
</tr>
<tr>
<td>H6</td>
<td>47.7</td>
<td>40.5</td>
</tr>
<tr>
<td>H7</td>
<td>44.7</td>
<td>31.1</td>
</tr>
<tr>
<td>H8</td>
<td>47.2</td>
<td>31.4</td>
</tr>
<tr>
<td>H9</td>
<td>51.8</td>
<td>40.4</td>
</tr>
<tr>
<td>H10</td>
<td>64.4</td>
<td>49.8</td>
</tr>
<tr>
<td>H11</td>
<td>60.9</td>
<td>40.6</td>
</tr>
<tr>
<td>H12</td>
<td>83.5</td>
<td>54.1</td>
</tr>
<tr>
<td>H13</td>
<td>62.3</td>
<td>48.2</td>
</tr>
<tr>
<td>H14</td>
<td>77.5</td>
<td>51.5</td>
</tr>
<tr>
<td>H15</td>
<td>72.7</td>
<td>48.8</td>
</tr>
<tr>
<td>H16</td>
<td>69.2</td>
<td>49.7</td>
</tr>
<tr>
<td>H17</td>
<td>66.3</td>
<td>45.8</td>
</tr>
<tr>
<td>H18</td>
<td>42.9</td>
<td>46.5</td>
</tr>
<tr>
<td>Pristine</td>
<td>95.4</td>
<td>52.7</td>
</tr>
</tbody>
</table>

Looking at Table 4.1, it is possible to notice that both water and diiodomethane contact angles are reduced after plasma treatment, implying increases in both the polar and the dispersive components of surface tension (the standard deviation is not reported in the table due to the fact that measurements with standard deviation higher than 2° were repeated). Moreover the increase in the polar component is, proportionally, much higher than the increase in the dispersive component of surface tension; this is compliant with the hypothesis of introduction of polar nitrogen-bearing functionalities on the surface. When looking at results, it is to be kept in mind that, for clearness and fluency of the discussion, only some data are reported here, which are representative of the many experimental parameters that were varied during testing. Considering plasma IDs going from H3 to H9, the discharge power at the electrode was gradually increased by fixing all the other parameters,
this allows determining the effect of the discharge power and of the dose on wettability and surface tension of the polymer.

Figure 4.1 allows to better understand and notice several phenomena:

- Increasing the corona dose, by means of an increase in the discharge power, always leads to a growth in the surface tension of the plasma treated polymeric material with respect to the pristine surface.
- With respect to the pristine material, the increase in surface tension is mainly related to the polar component, which supports the theory of the introduction of polar functionalities by plasma treatment in the described conditions.
- The effect of plasma treatment on surface tension and water contact angle are not monotonic, but an optimum is reached, beyond which the effect is opposite to the objective. For corona doses higher than about 2300 Wm\(^2\)/min, i.e. for condition H8 and H9, the effect of plasma is that of increasing water contact angle and therefore reducing surface tension. This phenomenon can be explained considering that during plasma treatment two competitive processes are occurring simultaneously: etching and functionalization (this is always true for the experimental conditions adopted during this research, but in different plasma atmospheres the situation can be slightly different). Therefore, below a given dose threshold, functionalization is dominating over etching, when the dose is raised, the amount of functionalization of the surface reaches its maximum, while the etching processes increase surface degradation with the formation of low molecular weight fragments and therefore also etching some of the functionalities [98–100].

Looking at these data, representative of the best results obtained, it is possible to state that the optimal plasma treatment condition is H7, if the aim of the process is to maximise surface tension and minimize water contact angle. Since the aim of the treatment is to promote adsorption of palladium and, therefore, adhesion of the metallic layer produced by electroless deposition, condition H7 was not the selected to proceed in the experimentation. This choice will be justified later in the discussion. The condition H5 was indeed selected both to perform ageing studies and as pre-treatment for metallization.
Since it was experimentally observed and confirmed by the literature [101,102] that the effect of plasma treatment decays in time, two different series of ageing studies were performed to better understand the mechanisms of the so-called hydrophobic recovery: a first study was made to understand whether hydrophobic recovery, i.e. the gradual increase of water contact angle in time after plasma treatment, is either governed by interactions of the surface with the atmosphere or by temperature. The second set of experiments was done to determine solely the temperature dependence of the decay.

In Figure 4.2, results of the first run of ageing tests are shown; where series A represents results for samples stored at room temperature and under vacuum, series B for samples stored at room temperature and pressure and series C for samples stored at -18°C under vacuum.

From these data, it is possible to affirm that:

- While for series A and B the surface tension gradually decreases in time after plasma treatment, for series C the effect of plasma is maintained unchanged for the whole period of observation. Moreover (Figure 4.2) the reduction of surface tension almost exclusively related
Results and Discussion

Solvay Specialty Polymers spa confidential information

to the polar component, while in all cases the dispersive component is roughly constant for the whole duration of the study.

- The variation of surface tension is comparable between series A and B, this is clearly expressed by the similar variation in time of the water contact angle. The analogous behaviour of the surface tension in indeed connected to the almost identical increase of water contact angle (Figure 4.3).

- From this information, it is possible to state that the process of hydrophobic recovery is not affected by vacuum while it is influenced by the temperature. Therefore it is proposed that ageing is a physical process not or only marginally affected by chemical interactions with the atmosphere surrounding the surface. In other words, no chemical reactions with the atmosphere seem to occur during the ageing process. On the other end, as proposed in the literature, hydrophobic recovery is believed to be caused by macromolecular rearrangements in the surface region, which “hide” the polar groups, introduced by plasma treatment, to reduce the surface energy. The thermal dependence of this process is indeed justified by the direct proportionality between the free volume (therefore chain mobility) and the temperature [103,104].

\[ \text{Figure 4.4 Effect of storage temperature on the water contact angle measured on plasma treated HALAR® 350 LC ECTFE.} \]

The second run of ageing tests was therefore performed to verify and have an insight on the thermal dependence of hydrophobic recovery, with the final objective of defining a mathematical correlation between the variation of water contact angle in time and temperature. Vacuum storage was not considered since no relevant effects were detected in the first set of tests. Results, regarding water contact angle values, are reported in Figure 4.4 and confirm the observations deduced from the first set of ageing experiments. Even though surface tension was calculated for all samples, only water contact angle is reported since previous experiments demonstrated that the decay of surface tension in time is due to its polar component. Being the polar component directly correlated to the water contact angle, the choice to highlight the influence of temperature on this property was made. Looking at the results it is possible to notice that ageing kinetic is highly dependent on temperature: while at
4°C the water contact angle is nearly unchanged after 87 days, at 80°C a plateau is reached after only 3 hours. This further confirms the hypothesis of molecular rearrangement at the surface to “hide” polar groups, which is faster if chain mobility is higher. To determine the mathematical correlation between WCA(t) and temperature a parallelism was performed with the shift factor used in the time-temperature superposition principle.

![Figure 4.5 Master curve of WCA(t) for plasma treated HALAR® 350 LC ECTFE, fitted to the results relative to storage at 22°C.](image)

In particular the idea was that of building a WCA(t) master curve therefore defining the shift factor \( a_T \) and the activation energy for the ageing process. Although not properly concerning hydrophobic recovery, the principle of time temperature superposition is related to the viscoelastic and microstructural properties of the polymer and therefore to the mechanisms that favour chain motion. If the ageing process is therefore linked to macromolecular rearrangement, it is reasonable to believe that the underlying kinetic correlations are, if not the same, at least similar to the ones governing viscoelastic mechanical properties, where the free volume plays a role of paramount importance. The master curve WCA(t) is reported in Figure 4.5, fitting was performed manually with respect to the curve relative to \( T_{\text{ageing}} = 22°C \). In this case error bars are not reported to avoid confusion in the representation. Besides small fluctuations, it appears that the curves are superimposable; moreover if the shift factor for contact angle is defined as follows:

\[
a_T = e^{\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)}
\]  

(4.1)

Where \( E_a \) has the meaning of an activation energy (J/mol), \( R \) is the universal gas constant and \( T \) and \( T_0 \) the temperatures in K, it is possible to validate the master curve verifying the consistency of the activation energy for different temperatures.

After empirically defining the shift factor for each curve with respect to the curve at \( T_0 \), i.e. 22°C, both a graphical and a mathematical check of the process were executed: if eq. (4.1) is true, then the graphical representation of \( \log(a_T) \) as a function of temperature should be linear and \( E_a \) should have the same value for each storage temperature.
Figure 4.6 confirms that the logarithmic representation of the shift factor as a function of temperature is linearly fitted. This, in turn, is reflected in the $E_a$ which is reported in Table 4.2, for the different temperatures. Also in this case the standard deviation is small.

Table 4.2 Summary of shift factors for the different storage temperatures with respect to the reference temperature (22°C) and the associated activation energy.

<table>
<thead>
<tr>
<th>Storage temperature (K)</th>
<th>Shift factor, $a_T$</th>
<th>Activation energy, $E_a$ (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>277.15</td>
<td>0.031</td>
<td>1899.7</td>
</tr>
<tr>
<td>288.15</td>
<td>0.275</td>
<td>1887.4</td>
</tr>
<tr>
<td>295.15</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>313.15</td>
<td>21.2</td>
<td>1887.1</td>
</tr>
<tr>
<td>328.15</td>
<td>190</td>
<td>1853.2</td>
</tr>
<tr>
<td>343.15</td>
<td>1700</td>
<td>1888.7</td>
</tr>
<tr>
<td>353.15</td>
<td>6200</td>
<td>1888.4</td>
</tr>
</tbody>
</table>

It is therefore possible to conclude that hydrophobic recovery after plasma treatment is mainly a physical process whose kinetic is affected by temperature. In particular higher temperature leads to faster ageing. Moreover it’s possible to build a master curve that, for example, allows estimating the time needed to reach a given water contact angle (and therefore a given surface tension) at a specific storage temperature. Consequently the relationship between the shift factor and temperature was defined according to an Arrhenius type law and the average activation energy was found out to be 1884.1 J/mol, with an error smaller than 1%. Finally it is possible to notice that the master curve (Figure 4.5) is not characterized by a simple sigmoidal shape, but shows a plateau at intermediate times. A similar behaviour could be expected at temperatures above the glass transition temperature (for HALAR® 350 LC, $T_g=85°C$), while this is observed (Figure 4.4) also at storage temperature as low as 55°C. This behaviour could be justified considering that hydrophobic recovery involves only the outmost layers of the polymeric sample, which have different chemical composition from the parent material before plasma treatment and are characterized by the presence of low molecular weight...
segments. As pointed out by the Flory-Fox equation [105], the transition temperature of the surface layers could be therefore lower than expected and this would justify the particular shape of the master curve.

4.1.1.2 Surface morphology – SEM and AFM

Characterization of the morphological modifications induced by plasma treatment on ECTFE was performed for two main reasons: first of all to determine the suitable plasma treatment conditions that cause no or marginal damaging of the surface (etching) and consequently to verify that the increased wettability, measured after plasma treatment, is exclusively related to chemical modifications and not to morphological alterations.

Two different techniques were adopted, i.e. scanning electron microscopy and atomic force microscopy, to compare the surface of the polymer before and after plasma treatment, performed in different conditions. It was demonstrated that, for the selected plasma processing parameters, the morphology of the polymer surface is not affected by plasma treatment. This can be noticed from both SEM and AFM imaging performed on samples treated in the H5 plasma condition (Figure 4.7).

![AFM and SEM images of pristine, (a) and (b), and plasma treated, (c) and (d), HALAR® 350 LC samples. Plasma treatment condition H5.](image)

From AFM, the roughness was measured to vary from 53.3 nm for the pristine material, Figure 4.7 (a), to 53.6 for the plasma treated surface, Figure 4.7 (b).

It is therefore possible to conclude that the increase of surface energy, measured by contact angle, is not affected by morphological modifications since the selected plasma parameters don't cause any morphological alteration.
4.1.1.3 Chemical modification – XPS

After determining the increase of surface energy and excluding contributions related to morphological modifications, it was necessary to assess nature and amount of chemical modification. Chemical characterization was needed, in primis, to confirm the presence of nitrogen bearing functionalities, and therefore to define the side effects caused by plasma treatment with N₂ on ECTFE. X-ray photoelectron spectroscopy was selected for this purpose due to its characteristics: plasma affects only the outmost layers of the polymer, therefore small penetration depths were required; moreover high sensitivity to light elements was also necessary to assess the entity of small chemical modifications.

Looking at Figure 4.8, it is immediately possible to notice that the photoelectron spectrum for the plasma treated material (plasma condition H5) is different from that relative to the pristine polymer. Two new components appear, at about 400 and 530 eV, which are respectively related to the presence of nitrogen and oxygen. The introduction of oxygen as a consequence of plasma treatment at atmospheric pressure is well known in the literature and can be caused by two phenomena: in the first scenario some oxygen is dragged by the moving film in the discharge zone and is therefore excited by the generator, therefore oxidation occurs during the discharge. The second scenario involves the so-called post oxidation, i.e. the reaction of residual radicals on the polymer surface with environmental oxygen, after the film has left the discharge zone [64,65,98,106]. The presence of oxygen, whose atomic amount is reported in Table 4.3, is probably due to a combination of these two processes.

<table>
<thead>
<tr>
<th>Composition</th>
<th>C (at%)</th>
<th>F (at%)</th>
<th>Cl (at%)</th>
<th>N (at%)</th>
<th>O (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>47.9</td>
<td>39.1</td>
<td>13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pristine</td>
<td>47.8</td>
<td>39.1</td>
<td>13.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Treated</td>
<td>54.2</td>
<td>27.8</td>
<td>5.2</td>
<td>4</td>
<td>8.8</td>
</tr>
</tbody>
</table>

Table 4.3 reports the atomic composition of pristine and plasma treated ECTFE, compared to the theoretical composition. It is possible to notice that the atomic composition, measured for the pristine material, is perfectly in line with the theoretical composition of the specific grade of HALAR® ECTFE.
used. Looking at the composition after plasma treatment, consistent reduction of the amount of chlorine and fluorine is associated to the insertion of nitrogen and oxygen. Moreover the relative amount of carbon is increased. This information can be gathered and further understood considering the high resolution lines for the single atomic species, in particular C1s, Cl 2p and F 1s (Figure 4.9).

Further considerations can be proposed looking at Figure 4.9: it is clear, form (b) and (c) respectively, that plasma treatment allows to reduce the content of both fluorine and chlorine. Moreover the relative reduction of chlorine is higher than that of fluorine; this is reasonable considering the difference in bond strength between C-F and C-Cl, the first being much stronger than the second [107]. The C-Cl bond is indeed the weaker of the polymeric chain and accordingly is the element showing the higher reduction in relative concentration after plasma. The C 1s line, (a), is highly affected by plasma treatment. The most evident effects include the decrease in the relative intensity of high energy components and an increase of the components at intermediate binding energy. This is consistent with the loss of fluorine and introduction of oxygen and nitrogen, which have a lower oxidative effect on the carbon than fluorine [108]. Also the shape of the main component at low binding energy is affected by plasma; this could be related to the formation of unsaturated bonds or to the presence of a less oxidizing environment surrounding some carbon atoms.

It is therefore possible to conclude that plasma treatment causes the desired chemical modification, with the introduction of nitrogen bearing functionalities, associated with a reduction in the content of chlorine and fluorine. The increase of surface energy is therefore caused both by the insertion of polar nitrogen- and oxygen-bearing functionalities and the reduction of the fluorine and chlorine content. As will be demonstrated later on, this chemical modification, associated with the absence of morphological alterations, allows achieving satisfactory palladium adsorption and therefore electroless metallization, without altering the roughness of the substrate.

### 4.1.2 Electrochemical metallization

After plasma treatment, ECTFE samples underwent electroless metallization and, in some cases electrolytic metallization. The easiest way to determine the effectiveness of plasma treatment was that of performing electroless metallization with copper and observing, at first, the homogeneity of the metallic deposit and afterwards the adhesion of said layer. Most of the plasma conditions, used during experimentation, did not give satisfactory results in terms of metallic deposit homogeneity, in
particular three different situations were encountered with copper electroless deposition (Figure 4.10):

(a) Independently on the metallization time the sample was not coated by metal or only small portions were covered.

(b) Independently on the metallization time discontinuous metal coverage was obtained but on the whole plasma treated area.

(c) At short times, lower than 1 min, the deposition appears homogeneous, exceeding a certain deposition time (which could vary form 40 s to 60 s) blistering occurs with the detachment of portions of the metallic deposit.

Usually these three situations were associated to different plasma treatment conditions. Simplifying the observations and referring to information reported in Table 4.1, it can be stated that: condition (a) was met when the corona dose was too low and therefore the increase of surface tension, associated to the amount of polar groups on the surface, was insufficient, e.g. plasma ID H14. The condition (b) implied that a certain amount of nitrogen functionalities was grafted to the surface after plasma, but their concentration was too low to assure a continuous deposit. In this case plasma parameters were usually close to the best values but further tuning was necessary, e.g. plasma IDs H3 or H4. Condition (c) was met at high corona doses, usually in plasma conditions with corona doses higher than the one giving the highest surface tension, e.g. plasma ID H8 and H9. Although not verified, this could be related to the damaging of the surface by the high doses, which leads to the formation of low molecular weight fragments. Even though sufficiently functionalized with nitrogen-bearing functionalities, the short polymeric chains could be easily disentangled by the internal stresses, related to hydrogen evolution and metallic layer growth, therefore leading to the formation of blisters that are eventually detached from the polymeric substrate.

Plasma treatment in the conditions from ID H5 to ID H7 gave satisfactory results in terms of metallic layer homogeneity and continuity, therefore further selection was performed basing on adhesion properties, determined by cross cut and bending tests. It is to be pointed out that selection of the optimal plasma treatment conditions was referred exclusively to copper, which, unlike silver deposition, is a proper electroless process based on a commercial plating line.

### 4.1.2.1 Metal adhesion – cross-cut and bending

Cross cut testing was used as the main tool to discriminate among plasma conditions giving good results in terms of metal layer homogeneity and continuity. Bending test was also performed but it
revealed to be much less significant than cross cut, since all tested samples withstood, without cracking, tests at the lower available bending diameter, i.e. 1.5 mm. Due to the poor relevance of bending tests, in discriminating among different plasma conditions, this paragraph is therefore focused on the results obtained during cross cut testing.

Cross-cut also revealed to be a pass or fail test: despite the classification given by the ASTM norm, which includes 6 adhesion classes depending on the amount of deposit removed by the adhesive tape, all samples demonstrated to fall either in the 5B or in the 0B adhesion class. In other words the metallic coating was either completely removed or totally unaffected by the pulling of the adhesive tape. This phenomenon gives rise to a consideration: plasma treatment was homogeneous on the whole polymeric surface and therefore, when the adhesion force, resulting from the treatment was overcome, the whole metallic deposit was removed. In order to improve the selectivity of the test, different tapes, with increasing adhesion force, were adopted during experimentation. Testing was therefore performed starting with the tape having the lowest adhesion force and moving to the next, up to the one having the highest adhesion (or to complete detachment of the metallic deposit). Only samples showing homogeneous and continuous copper deposits were characterized, this occurred for the specimens treated according to the conditions of plasma ID H5, H6 and H7.

All samples were coated with a metallic layer having thickness of about 200–250 nm, the deposition time being 180 s for copper and approximately 10 min for silver. Results for copper deposits, reported according to the plasma treatment ID revealed that:

- All samples passed the test (5B class) up to the tape with certified adhesion force equal to 4.4 N/cm.
- Samples plated after plasma treatment in the condition H7 failed (0B class) with the tape having adhesion force equal to 7.7 N/cm.
- Samples plated after plasma treatment in the condition H6 failed (0B class) with the tape having adhesion force equal to 9 N/cm.
- Samples plated after plasma treatment in the condition H5 passed (5B class) even with the tape having adhesion force equal to 9 N/cm.

For this reason the H5 plasma treatment condition was selected for all ageing studies and metallization tests on HALAR® 350LC ECTFE. Moreover, although not certain, the lower adhesion of samples that underwent plasma treatment in the conditions H6 and H7 could be due to two different
but related causes: the first reason could be the previously cited formation of low molecular weight chains at the surface, which have lower mechanical properties with respect to the higher molecular weight polymer [109] and therefore are more prone to fail under the applied load of peeling. Considering that the surface tension is actually higher for condition H6 and H7 than for condition H5, also the nature of the polar groups at the surface might play a role. As demonstrated form XPS data, a high amount of oxygen is incorporated even after plasma treatment in the condition H5. Increasing the dose, i.e. condition H6 and H7, it could be possible that the atomic ratio between grafted oxygen and nitrogen also increases, therefore without significant positive effects on palladium grafting. This, associated with the increasing amount of low molecular weight fragments, could justify both the lower adhesion noticed for condition H6 and H7 and the blistering issues noticed for conditions H8 and H9.

Regarding silver deposits, tests were performed only on samples treated with the H5 plasma condition, which was verified to be optimal with copper, since the aim was that of determining the best activation process. Comparison was therefore performed among samples produced according to series I, II and III of Table 3.10. Results demonstrated that:

- Samples belonging to Series I failed (0B class) with the tape having adhesion force equal to 2.4 N/cm.
- Samples belonging to Series II and Series III failed (0B class) with the tape having adhesion force equal to 4.4 N/cm.

Moreover, on samples belonging to Series I, subsequent copper electroless deposition on silver lead to the delamination of the metallic layer from the polymer, while for samples belonging to Series II and III copper coating was easily performed and the copper-silver layer demonstrated the same adhesion as the silver-only deposit. The low adhesion obtained with the internal activation process, based on SnCl₂, is reasonable since nitrogen functionalities, introduced by plasma, are known to interact with palladium but to inhibit tin chemisorption [52]. Therefore the silver layer, probably, is not properly bound to the polymeric surface but mostly precipitated as in the whole solution; the deposition occurring preferentially on the polymer due to the catalytic effect of Sn species physisorbed on the surface. On the other end, commercial activation, being Pd-based, assures that higher adhesion is present between silver and the polymeric substrate since Pd interacts with the nitrogen functionalities introduced by plasma treatment. Finally, Series II activation procedure was preferred since in implied fewer steps and gave better results in terms of deposit continuity. The internal activation solution is indeed supersaturated with SnCl₂ and some salt particles remain on the polymer surface even after rinsing, therefore causing some defects during electroless deposition.

4.1.2.2 Nucleation and Growth – SEM

Once the best plasma treatment conditions, i.e. plasma ID H5, and the best activation process for silver electroless, i.e. the commercial activation, were defined, studies were performed using SEM to determine the nucleation and growth mechanisms for both silver and copper. As reported in chapter 3, the deposition times considered for copper and silver are significantly different, due to the slower kinetics of the Ag electroless solution.
Looking at Figure 4.12, it’s possible to notice that after only one second of immersion in the copper electroless solution, the first nuclei start forming on the polymer surface. For longer deposition times, the density and dimension of copper nuclei increases, up to the formation of a dense metallic deposit after 10s. This implies that after the commercial activation process, the catalytic Pd clusters are active and mostly reduced to the metallic state. It is indeed mentioned in the literature that chemisorbed palladium needs to be in the zero oxidation state to be catalytic towards electroless deposition [54,58]. If Pd species are not properly reduced at the polymer surface before immersion in the electroless plating bath, an induction time is necessary for electroless deposition to occur. Moreover if Pd is in its oxidized state and the reducer of the electroless solution is not able to induce reduction of Pd$^{2+}$, the electroless deposition process won’t be able to initiate at the polymer surface.

Figure 4.13 SEM images of copper surface after (a) 10 s and (b) 180 s of electroless deposition.
Finally, looking at Figure 4.13, it’s possible to notice that increasing deposition time to 3 min, the density of the copper crystallites is increased and their morphology is different; also average grain size was measured to be slightly higher for longer deposition times.

In order to optimize deposition times, depending on the thickness requirements for the application of the metallized polymer, deposition rate studies were performed by means of cross-sectional SEM imaging.

Deposition rate studies were performed starting from 40 s of deposition time to assure that metallic layer was continuous and homogeneous. Results (Figure 4.14) indicate that, for the time going from 40 to 180 s, the deposition rate is mainly constant and approximately equal to 50 nm/min. For times lower than 40 s, the deposition rate appears to be higher, this can be justified considering that in the initial stages of deposition a transition between nucleation on Pd clusters and growth on the formed Cu nuclei occurs, and this may imply different kinetics. Moreover this is well known in the literature that the initial deposition rate for electroless copper is always higher than the subsequent steady state [110].

Similar nucleation and growth studies were also performed on electroless silver. In this case, due to the slower kinetics of the internally developed bath, the deposition times necessary for nucleation were higher. Moreover the identification of the actual initiation time was not easy and was affected by the plating solution temperature. Differently from the studies performed for copper, the deposition rate was not determined while the maximum achievable thickness was measured. This choice is justified by the intrinsic instability of the electroless silver baths, which is a long known issue of this system [111] and allows depositing only thin metallic layers before spontaneous Ag precipitation.

As can be seen from Figure 4.15, even at the lowest deposition time, i.e. 180 s reported in Figure (a), the surface is already covered with a dense layer of silver nuclei. The dimension of silver crystallites increases with deposition time. At the longest time considered, i.e. 720 s reported in Figure (d), the metallic grains lose the spherical morphology previously observed, Figure 4.15 (a) to (c), and merge therefore forming a denser metallic layer. The formation of dense silver layers is of paramount importance for the final application, since fully dense and continuous metallic layers are needed to reflect properly the solar radiation.
Figure 4.15 Surface SEM images (100 K magnification) of Ag deposits. Deposition time increases from (a) to (d).

All the results reported here are relative to the silver deposits obtained using the commercial activation line. It was indeed verified that not only the adhesion, but also the homogeneity of the metallic layer, are improved using the Pd based activation line with respect to the Sn based one. In Figure 4.16, it is indeed possible to compare the different surface morphology obtained with the two processes: it is easily noticed that uncovered portions as well as large clusters of poorly adhered and spongy silver are present when the Sn-based activation solution is used. Vice versa, the surface is homogeneous and well covered when the commercial activation line is used.

Figure 4.16 Surface SEM image of a deposit obtained with the Sn-based (a) and with the Pd-based commercial activation bath (b).
After optimizing all parameters, the highest thickness of silver that could be obtained before spontaneous precipitation in the solution was approximately 200 nm, Figure 4.17. Unfortunately, considering the low thickness and probably the limited adhesion of the metallic deposit, delamination occurred during sample preparation in liquid nitrogen, probably due to differential thermal contraction or thermal shock.

Copper layers, electrodeposited on electroless copper (see experimental details in Table 3.14), were analysed to determine deposition rate and surface morphology. It can be observed that crystallite size is smaller for electrodeposited layers than for electroless deposited copper (Figure 4.18 (b) and (c)): after 180 s the average crystallite size of electroless deposits was measured to be slightly higher than 100 nm, while the electrodeposited layer is characterized by a smaller crystallite size of about 50 nm. This is justified by the presence of grain refiners and brighteners in the electrodeposition bath. Finally (Figure 4.18 (a)), the electrodeposited layer was measured to be approximately 3.75 µm thick; it results in an effective deposition rate equal to 315 nm/min, which is in line with the theoretical deposition rate, calculated assuming cathodic efficiency equal to 95%, i.e. 312 nm/min.

4.1.2.3 Microstructural analysis – XRD

X-ray diffraction was performed on some samples to have an indication of the presence of preferential crystalline orientation and of the crystallite size, which was verified to be lower than 300 nm by SEM.
Figure 4.19 XRD spectra for electroless silver/copper bilayer (a) and electroless silver deposit (b) on ECTFE

Figure 4.19 reports two different XRD spectra acquired for electroless metallic deposits on ECTFE. In (a) the spectrum for a sample obtained by electroless silver deposition followed by electroless copper is shown, while in (b) the spectrum for a ECTFE sample coated exclusively with silver is reported. In both cases, no preferential orientation is observed for the metallic deposits. The crystallite size, calculated by Scherrer method, is approximately 210nm for Silver (for both samples) and 150 for copper.

4.1.3 Metallized ECTFE as flexible concentrator mirror

Metallized ECTFE films were finally characterized to have a proof of concept of the applicability of this process to produce flexible concentrator mirrors. Flexible mirrors are used as reflective elements in solar thermodynamic plants and their basic elements are (Figure 4.20):

- One or more polymeric layers, some characterized by high transparency, responsible for protecting the reflective metal from oxidation and atmospheric agents that could cause abrasion and staining.
- A metallic layer having high reflective properties in the solar spectral range, e.g. Ag or Al.
- One adhesive layer to attach the flexible mirror on the rigid parabolic support. Other adhesive layers can be present, e.g. between the reflective metal and the protective polymer.
These multi-layered films are adhered to rigid parabolic supports that have the role of supporting the mirror with the correct shape and orientation to concentrate the solar radiation on the thermal collector. Once damaged, these films can be replaced with lower costs with respect to the substitution of the whole parabolic structure.

Plasma treatment and electroless deposition on ECTFE could be applied to produce this element since:

- ECTFE is known for its high transparency in the solar spectral range and for its chemical resistance [112].
- Plasma treatment was demonstrated to allow electroless metallization on ECTFE assuring continuous and dense deposits with good adhesion levels.
- Plasma treatment was demonstrated not to increase surface roughness of ECTFE, which would detrimentally affect the reflective properties of the assembly.

For this reason, even if on a simplified system, exclusively composed of HALAR® 350 LC ECTFE and a metallic layer, a further specific characterization was performed, i.e. UV-VIS-IR spectrophotometry.

### 4.1.3.1 Spectral reflectivity – UV-VIS-IR spectrophotometry

In order to have an idea of the potential performance of plasma treated and metallized ECTFE as concentrator mirror, spectral reflectance was determined by spectrophotometry on several samples (Table 3.15). Both copper and silver were characterized as reflective layers since, in the early stages of research, only copper could be deposited with sufficient quality and adhesion. Therefore the following results should be seen as the gradual optimization of the design and of the production process of the metal-polymer reflective film.
Observing results, graphically reported in Figure 4.21, it is possible to observe first of all the improvement in reflectance moving from copper (CM1 and CM2) to silver (CM3 to CM6) as first metallization layer. Going in further detail:

- **CM1 and CM2**: electrodeposition allows to increase the total reflectance of the system of a small amount considering that the metallic layer is approximately sixteen times thicker in the case of the electrodeposited copper layer (CM2) with respect to the electroless-only metallic deposit (CM1).

- **CM3 and CM4**: due to the higher quality of the silver deposit that can be obtained with Pd-based activation process (CM4), with respect to the Sn-based activation (CM4), also higher reflectance values can be obtained. Moreover, due to the intrinsic properties of silver the performance is highly improved with respect to CM1 and CM2.

- **CM5 and CM6**: deposition of a copper layer on the back side, which was meant to protect silver from oxidation and to fill eventual unplated portions of the polymer surface, didn't appear to improve the reflectance properties of the polymer-metal bilayer. A motivation for this behaviour has not been clearly defined yet. Being copper spectral reflectance lower than that of silver, it might be that copper growth in the small porosities of the silver layer actually decreases the reflecting properties since it covers higher reflectance silver. This concept is emphasized in Figure 4.22, where copper deposition, filling the porosities left by silver, reduces the contribution of silver itself to the total reflectance of the metallic layer.
It is therefore possible to conclude that this process, although needing further development and optimization, could allow producing flexible concentrator mirrors with good reflectance.

4.2 KETASPIRE® KT-820 PEEK

The structure of this section is in line with the previous: after introducing the polymer, plasma treatment and its characterizations will be presented, followed by description of metallization results and of the final application, with the relative tests. Since the characterization procedure is the same and many results are analogous, the discussion is presented in a more concise manner with respect to the previous section, so that repetitions are avoided.

4.2.1 Plasma treatment

As for ECTFE, plasma treatment was performed on PEEK to introduce nitrogen bearing functionalities, therefore allowing palladium grafting and subsequent electroless metallization. Although already studied, plasma treatment of PEEK has been performed mainly at low pressure and with the main aim of increasing bonding adhesion, not to introduce specific functional groups on the surface [41,113,114]. Due to the absence of fluorine in the polymeric chain, forming gas was used exclusively for some tests that will not be reported here, since it did not show any significant improvement with respect to nitrogen gas alone. As stated for HALAR® ECTFE, also in this case it is necessary to look at the plasma treatment conditions in a quantitative perspective only if applied to the specific equipment used. Considerations regarding the effect of atmospheric plasma treatment on this polymer, deducted from the following results, are universally valid only under a qualitative perspective.

4.2.1.1 Contact angle and ageing studies

Due to handling reasons, all the studies relative to contact angle and ageing are referred to 125 µm thick KETASPIRE® KT-820 PEEK samples. The results can anyway be applied also to the 6 µm thick KT-820 films, since they are composed of the same polymeric grade and the total thickness of the samples is approximately three orders of magnitude higher than the chemical modification depth of plasma treatment. Being conducted contextually to the studies on ECTFE, also for PEEK the initial goal of plasma treatment was that of increasing as much as possible the surface tension, i.e. increase the wettability of the surface measured with water and diiodomethane. A representative selection of results, for different plasma treatment conditions, is reported in Table 4.4.

<table>
<thead>
<tr>
<th>Plasma ID</th>
<th>Contact angle (°)</th>
<th>Surface tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
<td>Diiodomethane</td>
</tr>
<tr>
<td>P1</td>
<td>51.38</td>
<td>27.86</td>
</tr>
<tr>
<td>P2</td>
<td>48.04</td>
<td>24.98</td>
</tr>
</tbody>
</table>
It is possible to notice that not all plasma treatment condition led to an increase in the surface tension of the sample, especially plasma ID P14, which, differently from all the other conditions, was performed in pressure control rather than in flow control and without He. This could have led to the formation of a highly inhomogeneous plasma discharge characterized by a mainly filamentary rather than glow regime, which is favoured by the presence of helium. Besides this exception, in all other cases the total surface tension of the polymer is increased. As verified for ECTFE, also in this case the relative variation of the polar component of surface tension is much higher than the increase of the dispersive component. This is in line with the proposed hypothesis that plasma treatment causes the grafting of polar functional groups on the surface of the polymer. According to the same experimental procedure used for ECTFE, once the preferred composition of precursor gas was determined, dragging speed and discharge power where varied until an optimal set of parameters was identified. In the case of PEEK, the best discharge gas flow was found to be 1 nL/min of nitrogen and 5 nL/min of helium. After some tests, a good compromise between dose and dragging speed was found fixing the speed at 4.5 m/min and varying the discharge power between 1000 and 4000 W.

The graphical representation of the results for the optimal set of plasma parameters (Plasma ID P1 to P7), reported in Figure 4.23, allows noticing a similar behaviour to the one observed on ECTFE. The polar component of surface tension gradually increases with the corona dose/discharge power up to a maximum value. Accordingly, the opposite is true for the water contact angle, i.e. a gradual decrease is observed down to a minimum. Differently from ECTFE though, it is not possible to state that if the
corona dose is increased beyond the optimal value (plasma ID P5) the effect of plasma treatment is opposite to the desired one, i.e. surface tension is decreased. Looking at the results the surface tension appears to reach a plateau at discharge power equal to 2500 W, with small fluctuations at higher doses. The reason for this difference is not clear but could be related to the different chemical nature of the two polymers. The higher surface energy is anyway obtained for plasma ID P5, therefore this condition was selected as optimal for the plasma treatment of PEEK. This combination of plasma parameters was indeed found to give the best results also in terms of metallization quality and adhesion. Comparing the results obtained on PEEK and on ECTFE it is therefore possible to highlight the further differences:

- The equivalent corona dose necessary to maximise surface tension is lower for PEEK than for ECTFE, i.e. approximately 1000 vs 3000 Wmin/m². This is certainly due to the different chemical structure of the two polymers, the presence of fluorine is indeed known to increase the chemical resistance and therefore also the resistance to plasma treatment.
- The highest surface tension achieved by PEEK after plasma treatment is higher than that of ECTFE, i.e. 73.9 vs 63.1 mN/m. This is correlated to the water contact angle that is as low as 25° for plasma ID P5 and only reaches 44° for plasma ID H7. Even in this case the chemical structure appears to be responsible. At the same time it must be kept in mind that the quality and adhesion of the metallic layer are not exclusively related to the value of the water contact angle or of the surface tension. Therefore, as was previously demonstrated on ECTFE, it is not straightforward that higher surface energy means higher adhesion of the metallic layer.

To study the process of hydrophobic recovery and understand its governing principles, two series of ageing studies were performed, as described in Chapter 3, with slightly different objectives. A first series of plasma treated samples was stored in four different conditions: at room temperature and pressure, at room temperature and low pressure, at low temperature (-18°C) and room pressure and at low temperature (-18°C) and pressure. The aim was to understand if the main parameter affecting ageing was temperature or the chemical interaction with the environment surrounding the polymer. The second series of samples was therefore stored at room pressure and at different temperatures to investigate exclusively the effect of temperature on the kinetics of hydrophobic recovery.
From Figure 4.24 and Figure 4.25, some conclusions can be performed on the process of hydrophobic recovery, which in turn affects the surface tension of the material:

- If plasma treatment mainly affects the polar component of surface tension, similarly during ageing the reduction in surface tension is entirely determined by the polar component while the dispersive is constant in time.
- No relevant difference is noticed, both at room and at low temperature, between the samples stored at low pressure and the ones stored at room pressure. Both surface tension and water contact angle profiles are indeed similar for samples stored at the same temperature, under different pressure conditions. This suggests that chemical interactions with the environment surrounding the sample do not affect relevantly the ageing process.
- While the samples stored at low temperature show no or limited variations in water contact angle and in surface tension, room temperature ageing causes a decrease in surface tension and therefore and increase in water contact angle. This suggests that the process of hydrophobic recovery is physical and its kinetics are affected by temperature, as also stated in the literature [5,6].
Once clear that the kinetic of hydrophobic recovery is influenced by temperature, the second series of ageing studies was performed to define, as done for ECTFE, the mathematical correlation between the increase of water contact angle in time and temperature. As previously illustrated for ECTFE, also in this case the study is performed on water contact angle (WCA), despite also diiodomethane contact angle was measured, since:

- WCA is directly correlated with the polar component of the surface tension of the polymer.
- The polar component of surface tension is the one affected during ageing.

In Figure 4.26 results are reported relative to the evolution of WCA in time after plasma treatment for different storage temperature; in this case the influence of low pressure was not considered, since it was demonstrated that its effect is negligible. It is possible to notice that increasing the storage temperature the kinetic of hydrophobic recovery is faster; therefore, the WCA rises faster if the temperature is higher. Thanks to the higher melting temperature of PEEK, it was also possible to consider higher storage temperatures with respect to ECTFE.
Since the expected direct proportionality is observed for the variation of WCA(t) with temperature, the results were elaborated to obtain a master curve. As explained during the discussion of results for ECTFE, the idea of building a master curve comes from the hypothesis that hydrophobic recovery results from macromolecular chain rearrangements, which are favoured increasing the free volume and therefore the temperature. The master curve, centred on the measurements performed on samples stored at 23°C, was obtained by manual shifting of the single WCA(t) curves to obtain overlapping.

Figure 4.27 Master curve of WCA(t) for plasma treated KETASPIRE® KT-820 PEEK, fitted to the results relative to storage at 23°C.

Figure 4.27 reports the resulting master curve. Error bars are not reported in this graph to avoid generating confusion in the representation. It is possible to observe that the curve is well fitted to a sigmoidal shape, with the only exception of a few points, whose misalignment can be justified with experimental errors. Once the shift factors, relative to the reference temperature (23°C), had been determined for each ageing temperature, equation (4.1) was verified both graphically and mathematically. If the production of the master curve is performed correctly the logarithmic representation of the shift factor (αT) as a function of temperature should be well fitted by a straight line.
It can be seen in Figure 4.28 that the points are well fitted by a straight line. Extending the elaboration of data, it is possible to calculate the activation energy of the process of hydrophobic recovery, i.e. $E_a$ in equation (4.1). A summary of the resulting activation energies, calculated for each temperature, is reported in Table 4.5. The resulting activation energy value is approximately the same for each ageing temperature. Therefore it is possible to state that the activation energy of the process of hydrophobic recovery on PEEK, for the plasma condition P5, is equal to 1265 J/mol with an error approximately equal to 1%.

<table>
<thead>
<tr>
<th>Storage temperature (K)</th>
<th>Shift factor, $\sigma_T$</th>
<th>Activation energy, $E_a$ (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>277.15</td>
<td>0.089</td>
<td>1257</td>
</tr>
<tr>
<td>288.15</td>
<td>0.37</td>
<td>1275</td>
</tr>
<tr>
<td>296.15</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>313.15</td>
<td>7</td>
<td>1277</td>
</tr>
<tr>
<td>328.15</td>
<td>33</td>
<td>1277</td>
</tr>
<tr>
<td>353.15</td>
<td>300</td>
<td>1258</td>
</tr>
<tr>
<td>393.15</td>
<td>5200</td>
<td>1235</td>
</tr>
</tbody>
</table>

Comparing the activation energy for PEEK and for ECTFE, a lower value is observed for the aromatic polymer with respect to the partially fluorinated. This was not expected considering the higher stiffness of the aromatic chain of PEEK. At the same time it is necessary to consider that the process of hydrophobic recovery is not taking place in the pristine material, but in the plasma treated outmost layers, whose chemical composition and structure are different from the theoretical ones. Considering that one of the proposed effects of plasma treatment is aromatic ring opening [115], this could lead to higher chain mobility and therefore lower activation energies. Moreover the calculated activation energy is specific for the plasma treatment condition adopted for each polymer, which led to different surface modifications for the two materials.

### 4.2.1.2 Surface morphology – SEM and AFM

Since there is not accordance in the literature regarding the effect of plasma treatment on the surface morphology of polymeric samples, some studies were performed to determine if plasma ID P5,
selected for the metallization process, causes morphological alterations to the polymer surface [41,116,117]. It is important to verify that plasma treatment does not alter surface roughness and morphology since contact angle measurements can be affected by this parameter [118]. Therefore the abovementioned results should be partially reconsidered if surface roughness was found to be altered by plasma treatment.

Both scanning electron microscopy and atomic force microscopy were used to compare the surface of the polymer before and after plasma treatment, so as to have qualitative and quantitative information regarding surface morphology.

Results, reported in Figure 4.29, demonstrate that plasma treatment, executed with the selected parameters (plasma ID P5), doesn’t alter the surface morphology of PEEK. From AFM measurements the average surface roughness was found to be 18.9 nm for the pristine material and 20.2 for the plasma treated sample. It is therefore possible to state that the variation in surface tension, measured by water contact angle is not affected by morphological alteration but is entirely connected to chemical modifications. To check the amount and entity of chemical modification, XPS was therefore performed on pristine and plasma treated samples.

### 4.2.1.3 Chemical modification – XPS

Surface analysis by XPS was done to verify and quantify the grafting of nitrogen bearing functionalities on plasma treated PEEK samples. Besides nitrogen grafting, plasma is known to etch the surface of polymers, generating low molecular weight fragments and, especially if performed in open air, to introduce oxygen functionalities. It is therefore the aim of XPS treatment to analyse the surface of the samples to understand the entity of these modifications to the chemical structure of the polymeric
molecules. XPS was selected due to the shallow penetration depth, approximately 10 nm, which is necessary when superficial plasma modification needs to be characterized.

![Comparison of survey spectra for pristine and plasma treated PEEK samples.](image)

**Figure 4.30** Comparison of survey spectra for pristine and plasma treated PEEK samples.

**Table 4.6** Theoretical atomic composition of PEEK compared to that measured by XPS on a pristine and on a plasma treated sample.

<table>
<thead>
<tr>
<th>Composition</th>
<th>C (at%)</th>
<th>O (at%)</th>
<th>N (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>86.4</td>
<td>13.6</td>
<td>-</td>
</tr>
<tr>
<td>Pristine</td>
<td>84</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>Treated</td>
<td>81.5</td>
<td>15.6</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Approximately 3% of nitrogen was grafted on the surface as a consequence of plasma treatment, the composition of the pristine material is slightly different from the theoretical probably due to minor contaminations on the surface that could not be eliminated with the cleaning procedure prior to XPS analysis. Differently from ECTFE it is difficult to determine the net contribution of plasma treatment since oxygen is present in the parent chemical structure of the polymer.
Looking at Figure 4.31, some hypotheses on the mechanisms of chemical modification can be proposed. Even if the relative amount of oxygen and carbon is not highly affected by plasma, it is clear that their chemical states have been modified. In particular:

- Considering the high energy shake-up component of the C 1s line (centred at approximately 291.5 eV), it is possible to notice a reduction in intensity. Since this component is related to the presence of aromatic rings in the polymeric chain, plasma treatment is believed to induce aromatic ring opening as proposed elsewhere [115,119].
- Looking at the comparison of the O 1s line, also the chemical state of oxygen is affected by plasma treatment. It is therefore possible to say that even if the amount of oxygen is nearly unchanged, the oxygenated species on the plasma treated sample are different from those on the pristine material. In particular a shift is observed to higher energy for the O 1s line in the treated material with respect to the pristine reference. This could be due to an increased amount of C=O with respect to C-O bonds.

### 4.2.2 Electrochemical metallization

As for ECTFE, after plasma treatment PEEK samples underwent electroless metallization and, in some cases, electrolytic metallization. Due to the requirements of the applications selected for metallized PEEK, only copper was considered. The effectiveness of plasma treatment was empirically determined performing electroless metallization with copper and observing, at first, the homogeneity of the metallic deposit and afterwards the adhesion of said layer. It was verified that if plasma treatment caused limited modification of polymer surface tension (WCA > 70°), satisfactory results in terms of metallic deposit homogeneity could not be achieved. At the same time, plasma treatment leading to high surface tension (WCA < 50°) did not imply necessarily the deposition of homogeneous and adherent metallic layers. In particular similar situations to ECTFE (Figure 4.10) were encountered also for copper electroless deposition on PEEK (Figure 4.32):
Results and Discussion

Figure 4.32 Examples of metal deposits obtained on samples plasma-treated in non-optimized conditions.

(a) Independently on the metallization time the sample was not coated by metal or only small portions were covered close to the kapton tape mask.

(b) Independently on the metallization time discontinuous metal coverage was obtained but on most of the plasma treated area.

(c) At short times, lower than 1 min, the deposition appeared mostly homogeneous, exceeding a certain deposition time (which could vary form 40 s to 60 s) blistering occurred with the detachment of portions of the metallic deposit.

These three conditions are usually met after different plasma treatment conditions. The experimental observation is qualitatively the same as that described for ECTFE in paragraph 4.1.2. Summarizing and adapting to PEEK what previously described, it usually happened that: (a) occurred when the plasma conditions were completely wrong and the surface tension of the sample was low (WCA > 70°). Situation (b) occurred when the plasma was able to modify the polymer surface but the surface concentration of nitrogenated functional groups was not sufficient. This, in turn, could lead to an amount of chemisorbed palladium clusters insufficient to obtain a continuous metallic deposit, after the electroless process. Finally condition (c) was met for corona doses higher than the optimal value, e.g. plasma ID P7. In this case formation of blisters, followed by delamination could be due to the presence of low molecular weight polymer chains that, although properly functionalized with nitrogenated groups, are not suitably entangled to the bulk of the polymer and therefore are easily detached by the stresses generated during metal deposition. Therefore among plasma IDs P1 to P7, reported in Table 4.4, only condition P4 to P6 lead to continuous and homogeneous copper deposits. While all other plasma treatments fell in one of the three categories reported above.

Besides electroless metallization, electrolytic copper deposition was performed both on 6 and on 125 µm thick PEEK films. Electrodeposition was executed only on samples treated in the plasma condition P5. Probably due to the small thickness deposited (never more than 4 µm of metal), adhesion and flexibility results, reported hereinafter, are valid both for electroless-only and for electrodeposited samples. For practical reasons cross-cut was performed only on 125 µm thick PEEK films.

4.2.2.1 Metal adhesion – cross-cut and bending

Cross-cut and bending were performed on metallized samples to determine the optimal plasma treatment conditions. Bending though revealed to be superfluous, since all samples that were coated with homogeneous metallic layers passed the test with the lowest bending diameter available, i.e. 1.5
Selection of optimal plasma conditions was therefore based on adhesion, resulting from cross-cut test. As occurred for ECTFE, also this test gave different results from the expectations: the test was indeed either passed with the highest adhesion class (5B) or failed with the lowest (0B). Although unexpected, this behaviour implies that plasma treatment is homogeneous on the whole surface and therefore, when the adhesion force is overcome, the whole deposit is detached from the polymeric substrate.

![Figure 4.33](a) 6 µm thick KETASPIRE® KT-820 PEEK film after Cu electroless in the A4 metallization line and (b) Cu plated 125 µm thick PEEK sample after cross cut test (5B with 9 N/cm tape)

Four tapes, with different certified adhesion strength, were therefore used, in order to improve the selection ability of this test. Testing was performed starting with the tape having the lowest adhesion force. If the test was passed the next tape was used, up to the one having the highest certified adhesion force (or to complete detachment of the metallic deposit). Due to the fact that samples showing homogeneous and continuous copper deposits were characterized, only specimens treated according to the conditions of plasma ID P4, P5 and P6 were tested.

Results, reported according to the plasma treatment ID revealed that:

- All samples passed the test (5B class) up to the tape with certified adhesion force equal to 4.4 N/cm.
- Samples plated after plasma treatment in the condition P4 and P6 failed (0B class) with the tape having adhesion force equal to 7.7 N/cm.
- Samples plated after plasma treatment in the condition P5 passed (5B class) even with the tape having adhesion force equal to 9 N/cm.

For this reason the P5 plasma treatment condition was selected for all ageing studies and metallization tests on KETASPIRE® KT-820 PEEK. Moreover, although not experimentally verified, the lower adhesion of samples that underwent plasma treatment in the conditions P4 and P6 could be due to two different causes:

- Plasma treatment in the condition P4 could lead to sufficient functionalization with palladium clusters to have a homogeneous deposit. At the same time the amount of nitrogenated functionalities could be insufficient to reach the same adhesion as samples treated in the plasma condition P5. The measured surface tension was indeed lower than for plasma ID P5, therefore suggesting a lower amount of polar, and therefore also nitrogenated, functionalities.
This leads to a lower density of palladium clusters and therefore fewer bonding sites between the polymer and the metal.

- The reason for the lower adhesion in the condition P6 could be the previously cited formation of low molecular weight chains at the surface, which have lower mechanical properties with respect to the higher molecular weight polymer [109] and therefore are more easily disentangled under the applied load of peeling.

4.2.2.2 Nucleation and growth – SEM

Once the optimal plasma treatment conditions were defined, i.e. plasma ID P5, some studies were done to characterize the nucleation and growth behaviour of copper on PEEK.

![Figure 4.34: Surface SEM images (40 K magnification) of copper nucleation on PEEK after (a) 1s, (b) 2s, (c) 5s and (d) 15s of deposition.](image)

The nucleation behaviour on PEEK appears to be the same observed on ECTFE: the first copper nuclei are formed after one second of immersion in the electroless plating solution. For longer deposition times, initially the surface density (b) and therefore the dimension (c) of copper nuclei increases, up to the formation of a dense metallic deposit (d). This implies that the catalytic Pd clusters are active and mostly reduced to the metallic state. It was demonstrated in many studies that chemisorbed palladium needs to be in the metallic state to be catalytic towards electroless deposition [54,58]. If Pd is present on the polymer surface in its oxidized state, after immersion in the plating bath, an induction time is necessary for electroless deposition to start.

Since electroless deposition kinetics are affected by the substrate only in the early stages, i.e. when Pd density affects the metal reduction process, and it was verified that no induction time was necessary for PEEK as for ECTFE, growth rate studies were not performed on PEEK. Results would indeed be redundant since, after nucleation, the growth rate is only determined by plating conditions and
solution, which were the same for both polymeric materials. Also regarding electrodeposition, the results obtained on ECTFE were considered valid also for PEEK.

### 4.2.2.3 Microstructural analysis – XRD

![XRD spectrum for electroless copper coated PEEK film (deposition 180s)](image)

Looking at the XRD spectrum in Figure 4.35, obtained on a copper coated PEEK film, it is possible to notice the presence of a broad peak at low angles, due to the semi-crystalline nature of the polymeric substrate. Moreover, no preferential crystalline orientations can be deduced from the relative intensity of the diffraction peaks. Finally the crystallite size, using Scherrer method, was calculated to be approximately 140nm.

### 4.2.3 Metallized polymeric diaphragms for micro-speakers

Although no universally accepted definition exists, micro-speakers are usually defined as speakers that have at least one dimension smaller than 15 or 20 mm, depending on the builders. Two main issues are connected to micro-speakers: the first, which, even to a lower extent, is in common with traditional loudspeakers, is heat dissipation; the second is the acoustic performance at low frequencies. The latter is strictly connected to the small dimensions of micro-speakers. Heating is critical because it leads to sound distortions, especially at low frequency, and may ultimately cause system failure [120].

![Picture (a) and Schematic representation of the main components of a moving coil micro-speaker (b)](image)

**Figure 4.35** XRD spectrum for electroless copper coated PEEK film (deposition 180s)

**Figure 4.36** Picture (a) and Schematic representation of the main components of a moving coil micro-speaker (b).
Due to its high mechanical properties and to the retention of such properties up to high temperatures, PEEK is used in the field of traditional moving coil micro-speakers as oscillating diaphragm, Figure 4.36. Thin films, 6 to 20 µm thick, are particularly used in this field. Consequently, to face the abovementioned issues, investigations were performed on 6 µm thick PEEK films coated with three different thicknesses of copper. The main aim was that of improving thermal dissipation properties of the diaphragm; subsequently mechanical properties were tested to determine the effect of the metallic coating.

### 4.2.3.1 Thermal dissipation – IR Thermography

According to the experimental procedure described in Chapter 3, the thermal dissipation properties of PEEK films coated with three different thicknesses of copper (Figure 4.37) were compared to those of the bare polymeric film.

![Figure 4.37](image)

**Figure 4.37** 6 µm thick PEEK films coated with (a) 250, (b) 750 and (c) 1100 nm of copper, defined as MS1, MS2 and MS3 in Chapter 3.

Before starting with experimentation a software simulation (Simulia Abaqus) was externally commissioned to validate the hypothesis of improved thermal conduction imparted by the metallic layer on the polymeric film. Also in this case a comparison was performed on a simplified system consisting in:

- Polymeric (PEEK) film with diameter 30mm and thickness 6 µm in contact with a metallic coil, which was used as heat source;
- Metallic coil in contact with the polymeric film: inner diameter 8mm, outer diameter 10mm, concentric to the polymeric film.

The comparison was performed between the bare polymeric film and the same coated with a 500nm thick copper layer, opposite to the metal coil. The following physical parameters were used for the two materials:

- KETASPIRE® KT-820 PEEK:
  - Specific gravity: 1.3 g/cm³
  - Thermal conductivity: 0.24 W/mK
  - Specific heat: 2.15 J/gK

- Metal film (copper)
  - Specific gravity: 8.96 g/cm³
  - Conductivity: 400 W/mK
  - Specific heat: 0.386 J/gK

Results (Figure 4.38), relative to an imposed temperature increase from 20 to 90 °C, indicate that the metallic layer, although opposite to the voice coil, improves the thermal conduction properties of the diaphragm. It can be noticed that the temperature distribution is greatly affected by the presence of
the metallic layer: for the bare polymeric film, temperature increase is limited to the region proximal to the heat source, i.e. the voice coil, while for the metallized specimen a more homogeneous thermal profile is obtained on the whole surface. This result, although coming from a simplified simulation, demonstrated that heat flux inside the film is highly increased when the metallic coating is present, therefore encouraging experimental activity in this direction.

![Temperature distribution and specific heat flux](image)

**Figure 4.38** Comparison of temperature distribution in °C (a) and specific heat flux in mW/mm² (b) for bare PEEK and copper coated PEEK.

Experimental activity gave similar results, even though the tests were performed in different conditions with respect to the simulation: the current circulating in the voice coil was controlled, therefore the temperature of the heat source was indirectly modulated. The metallic layer was faced to the voice coil, so that the measurement was performed on the same surface for all samples. Differences in emissivity among the samples would indeed lead to errors in the temperature calculated by the thermal camera during the measurement. Before starting with experimental activity, the emissivity of copper coated PEEK films was determined on the polymeric side, to assure that the value was the same for all samples. Results indicated that the emissivity, ε, in the IR was the same for all samples, i.e. ε = 0.91.
Figure 4.39 reports the IR images relative to the three metallized samples (increasing metal thickness from left to right) at thermal equilibrium with the heat source and power switched on. It is possible to notice that the maximum temperature on the film surface decreases when the metallic layer thickness is increased. Moreover, although direct comparison could not be performed with respect to the bare polymeric film (it is transparent in the IR wavelengths of the camera), the temperature of the voice coil was measured to be 75°C. Therefore, considering the low thermal conduction of PEEK it can be assumed that the maximum temperature of the bare film is the same as that of the voice coil, i.e. 75°C. The maximum temperature is therefore always lower when the copper coating is present with respect to the bare PEEK, and the temperature reduction is higher the thicker the copper layer.

Figure 4.40 Temperature profile for the three samples along the lines reported in Figure 4.39.

Elaborating information contained in the IR photographs, it was possible to gather detailed information on the thermal profile of the three samples at thermal equilibrium. Looking at Figure 4.40, it is clear that not only the maximum temperature decreases with higher copper thickness, but that the thermal profile is also more homogeneous for thicker metallic layers, indicating that thermal conduction and thermal dissipation are both improved by the metallization process.

Finally the cooling profile after switching off the power was investigated for the three samples. In this case continuous imaging was performed after the power was removed. Some photograms, at two different times for the three samples are reported in Figure 4.41.
Figure 4.41 IR Photograms of the three samples at 2 s after the power was switched off (a), (b) and (c), and after 38 s (d) (e) and (f). Metal thickness increasing from left to right.

Also in this case further information could be gathered after elaborating the images. In Figure 4.42, the cooling profiles for the three samples are reported. The qualitative thermal decline is the same for all samples and the three curves never intersect, with the samples having higher copper thickness demonstrating lower temperature for the whole duration of the test. The cooling difference appears relevant if the time to reach a given temperature is considered: for example sample MS1 needs 32 s to reach 45°C while sample MS2 and MS3 need 22 and 17 s respectively.

Figure 4.42 Cooling profiles for the three specimens, after the current circulating in the heat source is switched off.
It is therefore possible to conclude that plasma treatment and metallization could allow improving thermal dissipation of the oscillating diaphragms inside micro-speakers, with the possibility of tailoring the metal thickness depending on the requirements. The effect of the metallic layer is indeed that of reducing the maximum temperature for a given actuation current. A direct consequence of this effect is that increasing the copper thickness, the same temperature is reached in shorter times during cooling. Moreover, when looking at IR thermography images, it is necessary to consider that the area of micro-speakers diaphragms is much smaller than that of the specimens used (indeed similar to the dimension of the voice coil), therefore metallization would allow the temperature profile to be roughly homogeneous on the whole surface. Once the effect on thermal properties had been verified, mechanical testing was performed.

### 4.2.3.2 Mechanical properties – Micro-tensile testing

Due to the presence of the copper deposit, whose thickness smaller but is comparable to that of the polymeric substrate, the mechanical properties of the samples could be significantly different from that of the bare polymeric film. For this reason mechanical characterization was performed. At the same time the reduced thickness of the samples, both metallized and bare, made mechanical characterization with traditional equipment difficult or even impossible. Micro-tensile testing was therefore identified as optimal technique to characterize the specimens and compare the mechanical properties, in particular the tensile modulus.

Samples produced in the same experimental conditions as the ones used for thermal imaging were therefore characterized obtaining the stress strain curves reported in Figure 4.43.

![Stress-strain curves](image)

**Figure 4.43** Stress-strain curves obtained from several samples for each copper thickness and individual comparisons to the results for the bare PEEK film.
Before moving to data elaboration, some considerations can be done on the stress-strain curves. The following interesting behaviours could be identified:

- The slope of the curves, with some exceptions related to experimental errors, increased with the metallic layer thickness.
- MS1 samples (250nm of Cu) showed a stress strain profile similar to the pristine PEEK, even if shifted to higher stress values.
- MS2 and MS3 samples (750 and 100 nm of Cu respectively) presented an abrupt drop in the stress value followed by a plastic deformation plateau.

These observations can be better explained and clarified when considering also the in-situ images, reported in Figure 4.44.

![In-situ optical microscopy sequences performed during tensile testing.](image)

It was indeed noticed that two different failure behaviours occurred, depending on the thickness of the copper layer. Thin metallic deposits (samples MS1) didn't demonstrate abrupt failure but the formation of several transversal cracks whose number and dimension gradually grew with the deformation. On the other end, for thicker metallic deposits (MS2 and MS3), the abrupt drop in the stress strain curve coincided with the failure of the copper layer, with the formation of a single transversal crack. Moreover, while for MS1 samples the metallic layer appeared to adhere to the substrate even after failure, MS2 and MS3 samples showed delamination at the polymer-metal interface, where sample deformation was concentrated. It can be therefore proposed that, up to 250nm, adhesion of the metallic layer to the polymeric substrate was higher than its cohesion, while for higher thickness the opposite was true and therefore delamination occurs.
Moving to data post-processing, it was possible to determine the effective elastic modulus of the different specimens considering, in the elastic portion of the stress strain curve, the difference quotient of the stress over the strain and increasing the interval to reduce the effect of the noise, namely:

\[
E_i = \frac{\sigma(\varepsilon)_i - \sigma(\varepsilon)_{i+\Delta i}}{\varepsilon_i - \varepsilon_{i+\Delta i}} \quad (4.2)
\]

The operation was iterated, increasing \( \Delta i \), until the noise was reduced sufficiently (Figure 4.45) and the value of the elastic modulus was calculated as the average value of the difference quotient for the selected \( \Delta i \).

Finally the elastic regime of metal-polymer assembly was schematized according to a system consisting of two or three parallel springs having different elastic constant. MS1 samples were schematized using the two-spring model, while MS2 and MS3 using the three-spring model. This choice was related to the difference in grain size observed for the electrodeposited and the electroless-deposited copper layers. It is indeed known in the literature that the dimension of crystallites affects the mechanical properties of the metal. Smaller crystallites indeed increase toughness but decrease the elastic modulus [121,122]. It was therefore considered reasonable to associate electroless and electrodeposited copper to two springs with different elastic constant (Figure 4.46). The resulting effective modulus, \( \bar{E} \), was therefore expressed according to the following equations:

- For MS1:
  \[
  \bar{E} = \frac{E_{\text{PEEK}}t_{\text{PEEK}} + E_{\text{Cu ELD}}t_{\text{Cu ELD}}}{t_{\text{PEEK}} + t_{\text{Cu ELD}}} \quad (4.3)
  \]

- For MS2 and MS3:
  \[
  \bar{E} = \frac{E_{\text{PEEK}}t_{\text{PEEK}} + E_{\text{Cu ELD}}t_{\text{Cu ELD}} + E_{\text{Cu ED}}t_{\text{Cu ED}}}{t_{\text{PEEK}} + t_{\text{Cu ELD}} + t_{\text{Cu ED}}} \quad (4.4)
  \]

Where \( t \) is the thickness of the different layers and \( E \) their modulus. From these equations it was possible to define the experimental elastic modulus for PEEK, electroless copper (Cu ELD) and electrodeposited copper (Cu ED).
Results are reported in Table 4.7. The fact that similar results are obtained for the elastic modulus of electrodeposited copper both for samples MS2 and MS3, suggests that the adopted model is reasonable and compliant with the microstructural differences of the three layers.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Effective Elastic Moduli (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK</td>
<td>1.94±0.19, 4.09±0.65, 7.12±0.99, 8.96±0.37</td>
</tr>
<tr>
<td>MS1</td>
<td>1.94±0.19, -</td>
</tr>
<tr>
<td>MS2</td>
<td>55.65±3.39, -</td>
</tr>
<tr>
<td>MS3</td>
<td>44.99±4.91, 44.79±2.18</td>
</tr>
</tbody>
</table>

It is therefore possible to state that the electrochemically deposited layer affects the mechanical properties of the metal-polymer assembly. In particular the elastic modulus is increased proportionally to the metal thickness and depending on the microstructural properties of the metallic layer. Electroless copper appears indeed stiffer than electrodeposited copper, probably due to the larger average grain size. Moreover the metallized films are able to sustain higher loads than the bare polymeric films.

From these observations some considerations can be performed in the perspective of the final application. It was previously cited that an issue for micro-speakers is the obtainment of low resonant frequencies; it is also known from the literature that the resonant frequency of the diaphragm depends, among the others, from its thickness and from the stiffness to mass ratio\[123\. Specifically the dependence on thickness is expressed by:

\[
 f_s = \frac{1}{2\pi} \cdot \frac{h}{2a^2} \cdot \frac{E}{3\rho(1-\sigma^2)} \left[ \frac{E}{\rho(1-\sigma^2)} \right]^{1/2} \]  

(4.5)

Where \( f_s \), \( h \), \( E \), \( a \), \( \rho \), \( \mu_n \), and \( \sigma \) are the resonance frequency, the thickness, the Youg's modulus, the radius and the density of the diaphragm, the roots of the frequency equation and the Poisson ratio respectively. From the same equation another formula can be obtained, which expresses the dependence of the resonant frequency on stiffness and mass of the diaphragm:
Results and Discussion

\[ f_s = \frac{1}{2\pi} \left( \frac{S}{M} \right)^{1/2} \]  

(4.6)

Where \( S \) is the stiffness and \( M \) the mass on the diaphragm.

Given that the metallized films are able to sustain higher loads, the thickness of the diaphragm could be therefore reduced therefore decreasing the resonant frequency. An estimate can also be performed on the stiffness to mass ratio of the metallized samples with respect to the bare PEEK film. In particular Table 4.8 refers to the square root of the ratio between the effective modulus, \( E \), and the apparent density, \( \bar{\rho} \).

<table>
<thead>
<tr>
<th></th>
<th>( E ) (Gpa)</th>
<th>( \bar{\rho} ) (g/cm³)</th>
<th>( \sqrt{\frac{E}{\bar{\rho}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK</td>
<td>1.76</td>
<td>1.32</td>
<td>1.21</td>
</tr>
<tr>
<td>MS1</td>
<td>3.57</td>
<td>1.62</td>
<td>1.58</td>
</tr>
<tr>
<td>MS2</td>
<td>6.06</td>
<td>2.17</td>
<td>1.81</td>
</tr>
<tr>
<td>MS3</td>
<td>8</td>
<td>2.50</td>
<td>1.89</td>
</tr>
</tbody>
</table>

Therefore although increased by metallization, the effect on the specific stiffness is not dramatic, considering the possibility of reducing the total thickness thanks to the improved mechanical properties. Moreover the thermal dissipation is highly improved. Therefore, with further studies, a good compromise could be found between the thickness of the metallic and of the polymeric layers.

To conclude, it was verified that plasma treatment and electrochemical metallization could be applied to the micro-speaker market, with specific advantages in terms of thermal dissipation on the oscillating diaphragm and with limited negative effects on the resonant frequency.

4.2.4 Circuit Breakers

A circuit breaker is an automatically activated safety device that opens an electrical circuit in case of overcurrent. This prevents the system from irreversible damages related to excessive currents. Unlike a fuse, which needs to be replaced after each overload, the circuit breakers can be reset many times. The real sensor/actuator inside the circuit breaker is usually a bimetallic strip, which is composed of two metals having different thermal expansion coefficients. In case of overcurrent the bimetallic strip is heated and deflects, therefore breaking the circuit [124,125].

The idea, hereinafter presented, is that of using metallized polymeric films instead of bimetallic strips as switches inside the circuit breakers. The marked difference in thermal expansion coefficient between copper and PEEK could be indeed exploited, as occurs in the bimetallic strips, resulting in higher deflections. With respect to conventional bimetal stripes, the PEEK-Cu switch could be used as safety device when small voltages and currents are acting on the circuit, e.g. inside mobile phone chargers. It must be kept in mind that the results and discussion that will follow are just meant to be a proof of concept of the principle at the basis of thermal/electrical actuation of the polymer-metal bilayer. An extremely simplified experimental setup was indeed considered, which is not meant to simulate the real operating conditions of a circuit breaker. Results and considerations are therefore meant to proof that, through plasma treatment and electroless metallization, polymer-metal bi-layers
(potentially also multilayers) can be produced and that the thermal expansion coefficient difference could be used to produce sensors or actuators.

The PEEK/Cu bilayers, produced depositing copper layers of several thicknesses on 125 µm thick KT-820 PEEK films, where characterized to define both the thermal and the electrical response.

### 4.2.4.1 Electrical actuation of PEEK-Cu Switches

The samples produced in the conditions reported in paragraph 3.2.3 were tested to determine if, changing sample geometry and the thickness of the metallic layer, the actuation current ($I_{act}$) can be tailored.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>CB1a</th>
<th>CB1b</th>
<th>CB2a</th>
<th>CB2b</th>
<th>CB3a</th>
<th>CB3b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu thickness (µm)</td>
<td>1.51</td>
<td>1.51</td>
<td>2.14</td>
<td>2.14</td>
<td>2.77</td>
<td>2.77</td>
</tr>
<tr>
<td>$I_{act}$ (A)</td>
<td>0.6</td>
<td>0.85</td>
<td>1</td>
<td>1.5</td>
<td>1.4</td>
<td>2</td>
</tr>
</tbody>
</table>

Elaborating the data (Figure 4.47), it is possible to observe that the actuation current is a linear function of the copper layer thickness. This is reasonable considering that the electrical actuation is actually a thermal actuation, induced by Joule effect. Therefore metallic layer resistance, as well as heating by Joule effect, is decreased proportionally to the thickness. Moreover the slope of the straight line that fits the two series (where series “a” is relative to the samples named a, e.g. CB1a, and series “b” to the samples named b, e.g. CB1b) is affected by the geometry: longer switch length leads to a lower activation current, for the same metallic layer thickness, and a lower proportionality between the two variables.

![Graphical representation of the actuation current as a function of the copper deposit thickness. The name of the series (a and b) recalls the nomenclature of Table 4.9.](image)

From these data it is therefore possible to conclude that by tailoring switch geometry and metallic layer thickness, it is possible to modulate the activation current of the PEEK-Cu switches. Moreover, due to the simple design of the switches, failure was usually related to arching phenomena, that gradually led to the degradation of the contact zone. It could be possible to improve this limitation, simply by applying the conventional precautions usually adopted to prevent arching.
4.2.4.2 Thermal deflection of PEEK-Cu stripes

Thermal actuation tests were performed due to the fact that electrical actuation in circuit breakers is actually a thermal actuation, induced by Joule heating, and that technical data sheets of bimetallic stripes include information regarding the linearity regime and the thermal deflection curves [126]. Moreover, thermal sensing/actuation ability of PEEK-Cu bilayers could demonstrate the applicability of such devices to other fields, where bimetallic strips are already used.

As previously mentioned, when two materials with different thermal expansion coefficients are bonded together, thermal variations cause internal stresses to be generated leading to shape variations. In the simplest case of a bi-material stripe homogeneously heated, these internal stresses lead to bending with a radius that is related to geometry and temperature, according to the following equation [126]:

$$\frac{1}{R_T} - \frac{1}{R_{T_0}} = \frac{6(\alpha_2 - \alpha_1)(1 + m)^2}{3(1 + m)^2 + (1 + m \cdot n)(m^2 + \frac{1}{m \cdot n})} \cdot \frac{T - T_0}{s}$$

Where $R_T$ is the radius at temperature $T$, $R_{T_0}$ the radius at temperature $T_0$, $\alpha$ the thermal expansion coefficients of the materials (where material 1 is the passive component and material 2 is the active component), $m$ is equal to $t_1/t_2$ where $t$ is the thicknesses of the two materials, $n$ is equal to $E_1/E_2$ where $E$ is the elastic modulus of the materials and $s$ is the total thickness of the strip ($t_1 + t_2$). The active component is the one with the higher thermal expansion coefficient and the passive the one with the lower thermal expansion coefficient.

The experimental data are shown in Figure 4.48. Beyond 140°C irreversible system failure was observed, this is probably due to the glass transition of the amorphous phase, which occurs at about this temperature. It is possible to see that the deflection profiles are higher for higher passive layer (copper) thickness and also that the deflection is higher for “a” specimens than for “b” specimens, which is reasonable considering the difference in length. Both phenomena are in agreement with the theoretical model derived by equation (4.7).
To have a better feeling of the deflection behaviour of the specimens, Figure 4.50 reports results only for “CB3a” sample. It is possible to observe that the deflection profile is similar but not compliant with the model, i.e. theoretical 30 mm. In particular the experimental points are not perfectly fitted by a straight line and the slope of a fitting line would be higher than the theoretical one. At the same time though, the theoretical model (derived from equation (4.7)), applied considering a free length of 35mm, allows to fit better the low temperature behaviour of the sample. At higher temperature the experimental displacement is still higher than the one predicted by the model. Although not reported, a similar behaviour is observed for all samples.

Some considerations can anyway be performed:
• The theoretical displacement curve is calculated considering the mechanical properties, i.e. the elastic moduli, defined for copper and PEEK during micro-tensile testing. While there is confidence that the mechanical properties are similar for copper, some differences could be present for PEEK due to the significantly different thickness and, likely, production process.

• The theoretical prediction is applied considering that the elastic modulus of the two materials is constant over the thermal interval considered. This is not the case since, increasing the temperature in the considered interval, the elastic modulus of PEEK reduces. Therefore the displacement from linearity of the deflection profile could be due to the softening process of PEEK. This is confirmed by the upward deviation of the bending profile, which could be fitted considering that the elastic modulus of PEEK decreases with temperature in the high temperature range.

• Samples having free length equal to 30 mm were actually 40 mm long, with 10 mm clamped in the grips. Although not certain, deviations from the theoretical deflection profile could be related to the non-ideality of the fixed end constraint. Thermal stresses were indeed present also in the 10 mm of sample clamped between the two grips. Since the constraints of the fixed end were not ideal, this could have affected the total deflection of the specimen.

Even though further studies should be performed on the thermal deflection behaviour of PEEK-Cu strips, in order to clarify the deviations from the theoretical behaviour, the thermal response was qualitatively in line with the expectations. Together with the electrical actuation studies, it was possible to demonstrate that plasma treatment and electrochemical metallization allow obtaining polymer-metal bilayers that can be used as sensors/actuators both thermally and electrically activated/sensing.

4.3 SOLEF® PVDF

In this section, results and discussion are organized in a different way from the ones relative to ECTFE and PEEK. This modification is due to the fact that differently from the previous study cases, where a possible application was proposed starting from the technological solution, the technological solution was applied to solve an existing issue: pristine PVDF foams (SOLEF® 80000 PVDF) could not pass the smoke toxicity test, which needs to be successfully performed for their application in aerospace; therefore plasma treatment and electrochemical metallization conditions were optimized and applied to this material, in this particular form, to solve this problem. The results presented in the following are partly relative to SOLEF® 80000 and partly relative to SOLEF® 60512 because the aim is that of showing the approach used to apply the technical solution to the existing issue: the knowledge acquired during fundamental studies on SOLEF® 60512 could be adapted and applied to plasma treatment and metallization of SOLEF® 80000 PVDF. For this reason the results obtained on SOLEF® 60512 are hereinafter associated to the optimization process performed on SOLEF® 80000.

To go in further detail:

• Plasma treatment: plasma conditions used for PVDF foams were deducted from the ones optimized for PVDF plaques. Therefore results relative to XPS and contact angle studies are referred to SOLEF® 6051, while optical and SEM imaging were performed on SOLEF® 80000 to determine the effect of plasma on the foamed structure.

• Metallization: adhesion and bending test could not be performed on foamed samples; therefore results are presented and discussed for SOLEF® 60512. Nucleation studies were not performed since results obtained on moulded plaques would not be significant for foamed samples, characterized by a different surface morphology.
- Application: tests were performed exclusively on foamed samples.

It is possible to see that most results are complementary. This section of the chapter should be indeed read considering that the experimental approach has been engineering rather than academic.

### 4.3.1 Plasma treatment

In the case of PVDF, the utilization of forming gas was found to be more effective, in terms surface tension increase and metallization quality, than nitrogen gas alone. The beneficial effect of the addition of small quantities of hydrogen to nitrogen for plasma treatment of PVDF was indeed confirmed in the literature [127]. Optimal plasma treatment conditions were initially defined on SOLEF® 60512, i.e. on moulded plaques. Subsequently the best conditions (both using nitrogen and forming gas) were tried on foamed samples but, due to the different morphology, they had to be adapted and further optimized. Therefore the optimal plasma treatment conditions of SOLEF® 60512 are different from that on SOLEF® 80000. Optimal conditions, in the case of foamed samples, were selected considering both the amount of surface melting and the homogeneity of the metallic deposit.

#### 4.3.1.1 Contact angle and ageing studies

![Figure 4.51](image)

Figure 4.51 Polar and dispersive components of surface tension for pristine and plasma treated SOLEF® 60512 PVDF moulded plaques.

All these studies were performed on SOLEF® 60512 moulded plaques. Results are reported in Figure 4.51. It is possible to observe that higher surface tension is obtained when forming gas is used, while with N₂ similar results are obtained independently on the other plasma treatment parameters. In this case is not possible to define precisely a corona dose due to the geometry of the plasma source and of the system.

Both condition S6 and S8 gave satisfactory results in terms of surface tension increase. At the same time S6 resulted in a higher thermal load and stronger plasma treatment for the sample, due to the smaller distance from the plasma nozzle and higher duty cycle, which led to unwanted deformations of the moulded plaques. For this reason and for the result of metallization, which will be shown later, plasma ID S8 was selected for further studies on moulded plaques.
Only one set of ageing studies was performed on PVDF, to understand whether hydrophobic recovery, i.e. the gradual increase of water contact angle in time after plasma treatment, is governed by interactions of the surface with the atmosphere or by temperature. Therefore after plasma treatment in the condition S8 samples were stored in three different conditions, namely: at low pressure and room temperature, at room temperature and pressure and at low pressure and temperature (-18°C).

From Figure 4.52, some considerations can be performed on the process of hydrophobic recovery, which in turn affects the surface tension of the material:

- Plasma treatment mainly alters the polar component of surface tension. Similarly, during ageing, the reduction in surface tension is entirely determined by the polar component while the dispersive component is constant in time.
- No relevant difference is noticed between the samples stored at low pressure (B) and the ones stored at room pressure (A). The reduction of surface tension is indeed similar for both sets of samples stored at room temperature, under different pressure conditions. This suggests that chemical interactions with the environment surrounding the sample do not affect significantly the ageing process.

Results reported in Figure 4.53 show that while the samples stored at low temperature show no or limited variations in water contact angle and in surface tension, room temperature ageing causes a decrease in surface tension and therefore and increase in water contact angle. This suggests that the process of hydrophobic recovery is physical and its kinetics are affected by temperature, as also suggested in the literature [5,6].
4.3.1.2 Surface morphology – SEM and optical microscopy

Plasma jet causes localized heating of the substrates that are treated, since the gas temperature is higher than for DBD discharges. SEM and optical microscopy were therefore performed on foams to investigate qualitatively the entity of surface melting after plasma treatment. The aim was that of determining the plasma treatment conditions giving the best compromise between metallic deposit homogeneity and foamed structure collapse. In this section only samples plasma treated with the following parameters are shown, since these resulted in better metallic deposit quality:

- Voltage: 270 V;
- Frequency: 21 kHz;
- Duty cycle: 100%.

Figure 4.54 Optical microscopy images of (a) pristine PVDF foam and PVDF foams plasma treated in condition (b) F11, (c) F7 and (d) F12.
Results and Discussion

Optical microscopy images for the pristine foam and some significant samples are reported in Figure 4.54. The aim is that of showing that increasing the energy of plasma, i.e. reducing scan speed and distance and increasing the number of passes, surface deformation is increased. It is possible to observe that surface morphology is similar for all plasma treated samples and different from that of the pristine foam. Plasma treated samples show a shinier surface than the pristine specimen due to the collapse of micro-pores during heating. Moreover the central portion of the beads, i.e. the single foamed elements composing the piece, is melted more than their walls thus leading to the formation of valleys, which are deeper increasing the plasma energy. Finally at the highest plasma energy, Figure 4.54 (d), also the walls of the beads appear to be partially molten, and the central portions appear to be duller than samples F11 and F7.

![Optical microscopy images](image1)

Figure 4.55 SEM images of (a) pristine PVDF foam and PVDF foams plasma treated in condition (b) F11, (c) F7 and (d) F12.

To have a deeper understanding of the morphological changes at the microscopic level, SEM imaging was performed on the same samples. SEM images, reported in Figure 4.55, are all relative to central portion of the beads. It is first of all evident that beads are composed by smaller closed pores with thin walls. Images confirm what observed by optical microscopy: the increase of plasma energy causes gradual melting and collapse of the micropores. SEM images also allow explaining the optical appearance of the different samples. Going from the pristine specimen to F11 and F7, the micropores collapsed to form a flatter surface; when the plasma energy was increased, i.e. F7, further surface melting occurred, increasing roughness and exposing underlying micropores. From this analysis both plasma ID F11 and F7 were considered as acceptable from the perspective of surface melting. The optimal plasma treatment conditions were subsequently defined combining these results with the quality of electroless copper deposits, which is hereinafter discussed.
4.3.1.3 Chemical modification – XPS

X-ray photoelectron spectroscopy was performed on SOLEF® 60512 PVDF to determine the amount and entity of chemical modification induced by plasma treatment. Tests were performed on moulded plaques treated in the conditions of plasma ID S8, which was selected as optimal for metallization.

![Comparison of survey spectra for pristine and plasma treated SOLEF® 60512 PVDF samples.](image)

Looking at Figure 4.56, it is possible to observe that oxygen and nitrogen are introduced in the chemical composition of the surface as a result of plasma treatment. Moreover, as can be better appreciated in Table 4.10, the amount of fluorine is reduced.

<table>
<thead>
<tr>
<th>Composition</th>
<th>C (at%)</th>
<th>F (at%)</th>
<th>Cl (at%)</th>
<th>N (at%)</th>
<th>O (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>46.2</td>
<td>51.9</td>
<td>1.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Treated</td>
<td>49</td>
<td>41.6</td>
<td>0.7</td>
<td>2.9</td>
<td>5.8</td>
</tr>
</tbody>
</table>

From Table 4.10, it is also possible to observe that chlorine is present in both the pristine and plasma treated sample, this is due to the fact that this grade is a copolymer of VDF and CTFE. It is possible to notice that also the amount of chlorine is reduced after plasma treatment, similarly to what occurred on ECTFE. These results indicate that plasma treatment in condition S8 allows introducing the desired nitrogen bearing functionalities on the surface, with the collateral effect of incorporating significant amounts of oxygen due to post-oxidation and probably direct oxidation during plasma discharge. At the same time chlorine and fluorine are preferentially etched from the surface. All these effects justify the observed increase in surface tension. The amount of nitrogen and oxygen incorporated as a result of plasma treatment is lower for this polymer than for HALAR® ECTFE; the fact that also the surface tension levels, achieved after plasma treatment, are lower for PVDF supports the theory that increased wettability is related to the introduction of polar (nitrogen and oxygen containing) groups.

The chemical modification is also reflected in the shape of the C1s line of the XPS spectrum, Figure 4.57. The relative intensity of low and intermediate energy components of the C1s line is increased after plasma, meaning that a less oxidizing environment surrounds the carbon atoms. At the same time
the relative intensity of high energy component is lowered, reflecting the reduction in the amount of fluorine in the polymeric chains. These observations are compliant with the loss of highly electronegative fluorine and introduction of weaker bonds with oxygen and nitrogen after plasma treatment [127].

![Figure 4.57](image)

**Figure 4.57** Comparison of high resolution C1s line for pristine and plasma treated SOLEF® 60512 PVDF.

### 4.3.2 Electrochemical metallization

In this section results regarding both PVDF plaques and foams are reported. In the first case discussion is aimed at demonstrating how plasma treatment conditions affect the macroscopic morphology of the metallic deposit; in the second case results, in terms of metal layer homogeneity and surface coverage, are shown to justify the selection of the preferred plasma treatment condition (in accordance with surface melting observed by optical and electron microscopy). All results reported in this section are relative to electroless copper deposits, performed with the commercial solution. Also electrodeposition was performed on PVDF foams to produce thicker metallic layers for the smoke toxicity test.

![Figure 4.58](image)

**Figure 4.58** Photographs of SOLEF® 60512 PVDF samples, treated with different plasma conditions, after electroless copper metallization.
After performing electroless deposition with copper, it was observed that almost every sample fell into one of the three following categories, reported in Figure 4.58:

(a) The metallic deposit is inhomogeneous and discontinuous but adherent to the polymeric substrate. This condition was usually encountered when the sample underwent insufficient plasma treatment, e.g. plasma ID S7.

(b) The metallic deposit is homogeneous but blistering occurs and the adhesion to the polymeric substrate is poor. This situation usually occurred when excessive plasma energy was used, e.g. for plasma ID S8.

(c) The metallic deposit is homogeneous, continuous and adherent. This condition was verified for plasma ID S6; this condition was indeed selected as optimal.

Besides these three cases, some deposition experiments also led to total absence of metal deposit, meaning that the plasma conditions were completely wrong for the purpose.

**Figure 4.59** Photographs of PVDF foams after plasma treatment, in different conditions, and electroless copper metallization. Namely (a) was treated in the conditions of plasma ID F6, (b) of F11 and (c) of F7.

Considering SOLEF® 80000 PVDF Foams, visual inspection allowed to select the plasma treatment conditions giving the best results in terms of metallic deposit quality. Examples of the results are reported in Figure 4.59. Initial metallization tests were performed after plasma treatment in the conditions that minimized surface melting, e.g. plasma ID F6. This led to poor or absent metallic deposits as shown in Figure 4.59 (a). In (b) a sample is shown metallized after a more aggressive plasma treatment, i.e. plasma ID F11, which caused limited surface melting (Figure 4.55 (b)). The metallic deposit is improved but still not extended to the whole surface. Finally the optimal plasma treatment condition was found to be F7, which allowed obtaining metallic deposits as the one reported in Figure 4.59 (c). Also other plasma conditions, as plasma ID F12, gave similar metallic deposits but were discarded due to the excessive surface melting.

### 4.3.2.1 Metal adhesion – cross-cut and bending

These characterizations were performed exclusively on moulded plaques due to limitations related to the surface morphology of foamed samples. Differently from the other polymeric samples, in this case only one plasma condition was found to give homogeneous and continuous metallic deposits, i.e. plasma ID S8. This is probably also related to the lower number of tests performed on this material.

As noted also for ECTFE and PEEK, bending test was passed even with the smallest bending diameter available, i.e. 1.5 mm. Cross-cut tests were performed, as described previously, with adhesive tapes having different certified adhesion forces in order to have more information on the adhesion level of
the metallic layer. Samples plated after plasma treatment in the condition S8 failed (0B class) with the tape having adhesion force equal to 9 N/cm.

### 4.3.3 Metallized foams for aerospace – flame resistance test

The utilization of PVDF foamed panels in aerospace is aimed at lightweighting assuring good thermal and acoustic insulation, while maintaining good mechanical support to the structure of the aircraft. When a new material/component is proposed to the aerospace industry, strict requirements must be met. Among the others, flame resistance test must be passed, i.e. the amount of toxic compounds in the fumes produced during testing must be lower than specific threshold values. Pristine PVDF foams could not pass this test due to the generation of amounts of HF higher than the limit. The deposition of a metallic skin was meant to protect the foamed polymer from direct flame, distributing the localized heat on a wider surface and reducing direct chemical degradation by the flame.

![Figure 4.60](image)

**Figure 4.60** Pristine PVDF foamed samples after testing. Namely (a) 8 mm thick, (b) 13 mm thick, (c) 30 mm thick and (d) 30 mm thick removed from sample holder.

Figure 4.60 reports pictures of the different samples (see Table 3.7) after testing. It is possible to notice that the foams were completely melted and mostly blackened, this indeed caused the generation of unwanted HF, namely:

- 8 mm: HF was 235 ppm
- 13 mm: HF was 320 ppm
- 30 mm: HF was 1000 ppm

![Figure 4.61](image)

**Figure 4.61** Metallized PVDF foamed samples after testing. Namely (a) 8 mm thick, (b) 13 mm thick and (c) 30 mm thick after breaking the metallic skin to show the polymer.

Figure 4.61 shows some of the metallized samples after testing. It can be noticed that, despite oxidized, the metallic skin is intact, and moreover the foam is not completely melted as occurred for pristine samples. Most importantly no blackening occurred and this is reflected in the content of HF.
Independently on the thickness of the metallic layer and on the geometry of the sample no HF (0 ppm) and more generally no smoke was generated. Therefore the metallization process allowed to highly improve the performance of PVDF foams in this test. In order to limit weight increase and production process complexity therefore electroless-only copper deposits allow obtaining excellent results.

In this section it was therefore possible to demonstrate that plasma treatment and metatization can be applied to tri-dimensional objects, that know-how can be extended with relative small efforts to different grades and forms of the same polymer with good results and that a thin metallic skin can lead to paramount changes in performance and properties of foamed PVDF samples. In the future the performance of thinner copper layers could be investigated and samples could be further characterized.

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Results and Discussion


Conclusion and Outlook

In this work the application of open-air atmospheric-pressure plasma treatment (from now on referred to as plasma treatment) and electrochemical metallization was studied on advanced polymers. The association of plasma treatment and electrochemical metallization is not innovative per se, but, as demonstrated in the literature review, most studies were performed on commodity polymers and in many cases using low pressure or controlled atmosphere systems. The utilization of industrial level open air plasma equipment to pre-treat advanced polymers for metallization is therefore innovative. Despite this thesis works is focused on a limited number of materials and applications, the ongoing research and the potential applications of this couple of technologies is much wider.

In this manuscript it was demonstrated that plasma treatment can successfully replace chemical etching with hazardous chemicals, e.g. on PEEK, and allow performing electrochemical metallization on fluorinated polymers, e.g. ECTFE and PVdF, with outstanding adhesion. The fundamental step that allows having continuous and homogeneous metallic deposits with good adhesion is the tuning of plasma parameters in order to:

- Introduce active nitrogen-bearing functionalities that are able to chemisorb palladium during the activation process;
- Minimize degradation of polymeric chains that lead to the formation of low molecular weight fragments.

Plasma treatment parameters must be therefore tuned to obtain the best compromise between these two phenomena, which simultaneously occur when the polymer surface is exposed to plasma. It was shown that the optimal (or better, the best that could be determined during research activity) plasma treatment depend not only on the chemical structure, but also on the form of the polymer. For
example, the plasma parameters identified as optimal for moulded PVdF plaques needed to be changed when moving to PVdF foams. The influence of polymer chemical structure is reasonable since the main effect of plasma treatment is chemical modification, which is affected by bond strengths within the polymeric chain.

It was demonstrated that plasma treatment, due to the grafting of polar (oxygenated and nitrogenated) functional groups, causes the surface tension of the polymers to increase. The polar component of surface tension is mainly affected by plasma treatment and is the main responsible for the process of hydrophobic recovery. This Phenomenon was studied by means of ageing tests performed in several conditions. It was concluded that, according with the literature, hydrophobic recovery is mainly a physical process related to the rearrangement of plasma modified macromolecules to "hide" polar groups from the surface. It was indeed verified that this process in not affected by vacuum and that it is temperature dependent. Moreover, for PEEK and for ECTFE, it was possible to build water contact angle master curves therefore defining the activation energy for the process of hydrophobic recovery. Moreover the increase in wettability and surface tension is to be completely attributed to chemical modification since no relevant morphological alteration were noticed, by SEM and AFM, on PEEK and on ECTFE. Further studies could be performed in this framework to confirm the possibility of building master curves and to determine whether the activation energy is affected by the plasma treatment parameters (and therefore by the entity of chemical modification).

Metallization results indicated that the best deposit quality and adhesion did not necessarily coincide with the plasma treatment conditions imparting the highest surface tension to the polymeric substrate. This was believed to be due to the competition between functionalization and chain degradation; this may lead to the formation of low molecular weight fragments that could easily be removed from the surface before or during the metallization process. Cross cut and bending test confirmed the high adhesion levels and flexibility of the metal coating. Further studies could be performed in this framework to have a higher resolution on the adhesion levels of the metallic layer obtained after this process. For example peeling test could be performed in order to have a precise value for the adhesion strength.

Moving to the applications, it was possible to demonstrate that this process can be applied to the production of devices where the properties of the polymer layer need to be associated to that of a metallic layer. At the same time, it must be kept in mind that the aim of this thesis is only to provide a proof a concept of the applicability of the process to different devices. In all cases further work should be performed to obtain the final product. In particular:

- Halar films coated with copper and subsequently with silver were proposed to be used as flexible solar concentrator mirrors. It was possible to obtain both good adhesion and light reflection properties. Besides the production of a full flexible mirror, which implies the introduction of other components as back side adhesives and anti-scratch front layers, also the development of silver electroless baths, able to produce metallic deposits with higher adhesion, would be necessary.
- Copper plating of PEEK was proposed for two different applications, i.e. micro-speaker diaphragms and circuit breakers. In the first case, thermal conduction and dissipation were verified to be highly improved by means of IR thermal imaging. Perturbation of mechanical properties, e.g. the specific elastic modulus, was also verified by means of micro-tensile testing. Further studies could be performed using the metallized diaphragm in a real speaker to directly measure the effect of metallization on acoustic properties. Optimization of the metallic
thickness could be subsequently performed to compromise between mechanical and thermal properties. It was moreover demonstrated that polymer-metal bilayer stripes can be used as circuit breakers, also referred to as switches, in low voltage and current applications. Altering the geometry and the thickness of the two materials, it is possible to modify the actuation current. Thermal response was also determined but further studies should be performed in this field, especially to improve the prediction model and the experimental setup. At the same time it was demonstrated that polymer-metal bilayers can be used as sensors/actuators under electrical and/or thermal stimuli.

• Finally thanks to the know-how acquired during research, it was possible to apply this process in a short time frame to solve an existing issue. Metallized PVdF foams could indeed pass the flame resistance test (pristine foams could not) that is necessary for their application in aerospace. This was a demonstration of the value of this process to actual industrial issues.

Although this thesis only investigated a small portion of the potentialities of this technology, it was demonstrated that plasma treatment and electrochemical metallization can be a valid alternative to existing technological solutions and can open new industrial opportunities. This is confirmed by the interest demonstrated by Solvay Specialty Polymers in this project.
I’d like to thank, first and foremost, my supervisor, Professor Luca Magagnin, for his constant support, for his advices and for the trust he always demonstrated in my capabilities, pushing me to overcome the limited boundaries of my knowledge.

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I’d like to express all my gratitude to my Friends - I’m sure each of them will understand that I’m referring to him/her - because they helped me to understand, and still recall when I forget it, that passing an exam, succeeding in an experiment or achieving professional goals is nothing compared to spending some time with a real Friend.

I’d like to express the most felt thanks to my family, for teaching me that no matter how smart or how good you are in your studies and in your work, if you are not humble and don’t respect your neighbour, you will always loose as a person.

Last but not least I’d like to thank Elodie for taming me as the rose did to the Little Prince. I’d like to thank her since she made me understand that joy is brighter and pain is milder when shared with someone special.