Electrochemical Strategies for the Strengthening of Polymer−Metal Interfaces

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Polymers have been widely used for the protection of metals against corrosion and for improving the performance of structural adhesive joints. In this contribution, the weakness and short-term durability of these polymer–metal interactions and some common approaches for alleviating this problem are briefly reviewed. Among the existing techniques, electrochemical processes offer the advantage of controlled interfacial reactions. Promising results have been reported by Stratmann et al. and Lécayon et al., who have emphasized the interest and opportunity to create strong chemical bonds between the organic coating and the metallic substrate. Their work is discussed in this review, along with results recently obtained in our group.

1. Polymer−Metal Associations

Suitable combinations of metals and organic polymers play an increasingly important role in modern technology. One of the most direct examples is the use of polymers as glue for metal objects. The adhesive bonding for structural joint formation has several distinct advantages over more conventional joining techniques: (i) the lack of local stress concentration, in contrast to riveted joints; (ii) the limitation of electrolytic corrosion when different metals are joined; and (iii) easy design and construction techniques.[1] Furthermore, polymer coatings have the potential to protect metals from chemical corrosion by acting as barriers.[2,3] Generally, only permanent polymer−metal interactions can delay delamination when the environment contains very aggressive species (e.g. ions, oxygen, water), prone to electrochemical and chemical attack.[4−8] As a rule, as long as the coating adheres strongly to its substrate, the metal is efficiently protected from any corrosion processes. Conversely, any defect or discontinuity in the coating (e.g., as a consequence of mechanical stress), makes the metal accessible to the electrolyte, thereby forming an aqueous corrosion cell between this defect and the delamination front. It is generally accepted that corrosion does not play a decisive role in the loss of adhesion in metal−polymer joints, but that this problem is rather a post-failure phenomenon.[9−11]

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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Figure 1 schematically shows the primary corrosion reactions that occur in the case of delamination of an epoxy coating from a steel substrate. The anodic reaction is the dissolution of iron, which is expected to occur in any location where an aqueous medium is available to accept ferrous ions, for example, within a defect of the polymer coating. The primary cathodic reaction is the formation of hydroxide ions by the reduction of oxygen at the metal−polymer interface. Five components are required for this reaction to occur: water, oxygen, electrons flowing from the local anode to the local cathode, positive counterions (e.g., Na^+) for the generated OH^- anions, and metal oxide, which is an active catalyst in the reduction reaction. All these components are commonly present beneath the coating at the boundary of the defect. In the case of weak metal−coating interactions (hydrogen bonding between an hydrated metal oxide and the epoxy resin in Figure 1), the cathodic reaction is responsible for the detachment of the polymer from the metal. As delamination proceeds, the cathodic site moves, remaining just in front of the debonding region.

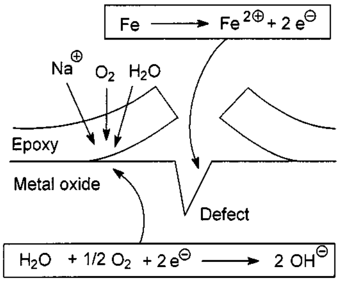


Figure 1. Schematic diagram of the delamination mechanism initiated by corrosion in a steel/epoxy coating system[11]

Numerous methods have been proposed to limit the extent of this loss of adhesion initiated by corrosion,[11] the general principle being to prevent at least one of the required components from being present at the metal−polymer interface. Although the fundamentals that govern the corrosion processes under protective coatings are generally well understood, little progress has been made to successfully prevent their occurrence. Nevertheless, these methods rely upon simple chemical and physical concepts that are easily implemented by adding at most one step in the coating process. As representative examples of these techniques, let us mention (i) the use of fluorinated polymers that limit the extent of water permeation usually occurring through most organic coatings;[3−11] (ii) the addition of fillers in order to reduce both the oxygen permeation rate[12] and internal stresses through the polymer layer; or (iii) metal pre-treatments by corrosion inhibitors, which is the most commonly used method. A thorough review of inhibitors, together with their corrosion-retarding mechanism, has been published by Trabanelli and Carasitti.[13]

Although corrosion of the metal substrate plays an important role in the delamination process, it must be stressed that joint delamination is essentially initiated by weak polymer−metal interactions.[11,14] To solve this problem in many technological applications, stable and porous oxide layers are prepared on top of the metal by adequate pretreatment (chromic acid etching, phosphoric acid anodizing, etc.)[11,15] before coating with the polymer. This technique can impart a reasonable durability upon exposure to environmental attacks. The origin of the good adhesion between this inorganic conversion coating and the polymer is not well understood. It is probably due to mechanical interlocking between the polymer and the porous surface oxide of the substrate. However, the formation of strong chemical bonds between the substrate and the polymer, instead of weak secondary interaction forces, is expected to be more efficient in inhibiting any electrochemical reaction at the interface. Although physical treatments, such as plasma polymerization,[16,17] are of great interest, this review will mainly focus on electrochemical techniques. Their advantage over surface plasma modification is essentially that controllable reactions are involved. Furthermore, electrochemistry is a valuable technique for the polymerization of various monomers at metal surfaces, which allows for the broadening of the search for improved polymer−metal interactions. In this respect, two main electrochemical strategies have been proposed to create strong chemical bonds between organic polymers and metals.

The first strategy devised by Stratmann[18] consists of three main steps (Figure 2). The metal surface is first cleaned carefully (step 1) in order to make reactive centers (A) available. A monolayer of specially designed (A−B) molecules is then chemisorbed onto this surface (step 2), and finally a polymer is covalently bonded to these immobilized molecules (step 3).

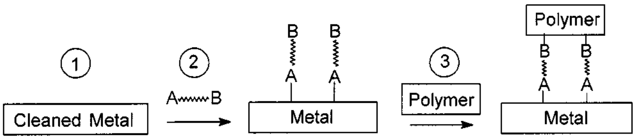


Figure 2. Reaction scheme proposed by Stratmann,[18] in which "cleaned metal" refers to the surface covered by a monolayer of sites A after electrochemical reduction

The second strategy is based on the pioneering work by Lécayon et al.,[19] who proposed that direct "grafting" of a polymer onto a metal can be achieved by controlled cathodic electropolymerization of the parent monomer (Figure 3).

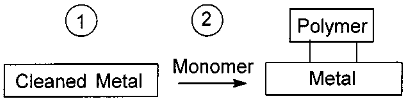


Figure 3. Reaction scheme proposed by Lécayon et al.[19]

2. Organic Molecules as Anchors for Further Polymerization

2.1. Chemical Approach

During the last decades, chemical modification of the surface of metals and carbon has been widely investigated.[20−22] It is well known that metal surfaces can be pre-treated, for example, by chromic acid etching, in order to remove old oxide layers and to generate new ones that exhibit well-defined microdepressions acting as efficient mechanical interlocking sites.[11,15] This renewed surface is favorable not only to physisorption, but also to chemisorption as a result of secondary interactions (e.g. hydrogen bonding) between polar groups on the polymer and hydroxy groups on the metal oxide surface. These hydroxy groups have been widely exploited in order to anchor "chemical coupling agents," which are most often low molecular weight multifunctional molecules (organosilanes) able to anchor the polymer coating to the metal substrate through water-resistant covalent bonds.[11,23] It is, however, a delicate task to generate a perfect monolayer of the coupling agent attached to the substrate surface. Usually, several layers of physisorbed coupling agents are deposited on the surface from the cast solution. Since these layers are cohesively weak, fracture is generally observed in this region, as confirmed by Auger and X-ray photoelectron spectroscopy (XPS).[24]

2.2. Electrochemical Approach

The approach proposed by Stratmann[18] is an improvement of the aforementioned concept. As a model system, this author used polycrystalline iron (cleaned of any organic impurities) as substrate and thiols (e.g., *n*-decanethiol: *n*-$C_{10}H_{21}SH$) as model coupling agents. Thiols are indeed reported to strongly chemisorb onto the clean iron surface by formation of Fe−S bonds as result of S−H bond cleavage. It has been shown that OH groups present on the metal oxide surface cannot be displaced by the thiol groups, whereas stable bonds are formed between clean metals and thiols, as confirmed by X-ray photoelectron spectroscopy.[18,25−26] The first step of the process is thus the careful removal of the metal oxide layer from the surface under electrochemically controlled conditions. Figure 4 shows the cell used for the preparation of the iron surface and the binding of the thiol onto this surface. The iron surface, free from any oxide layer, is prepared by polarization in perchloric acid (1 M, $HClO_4$) at a potential of −0.72V vs. the standard hydrogen electrode (SHE). Under these conditions, the metallic state of the iron surface is thermodynamically stable.[25] In the next step, the thiol is poured onto the surface of the aqueous electrolyte and the iron electrode is slowly pulled out of the electrolyte through this organic layer, under controlled potential (Figure 4). The hydrophilic thiol groups (SH), which are preferentially oriented towards the polar electrolyte, are transferred to the new iron/thiol phase boundary.

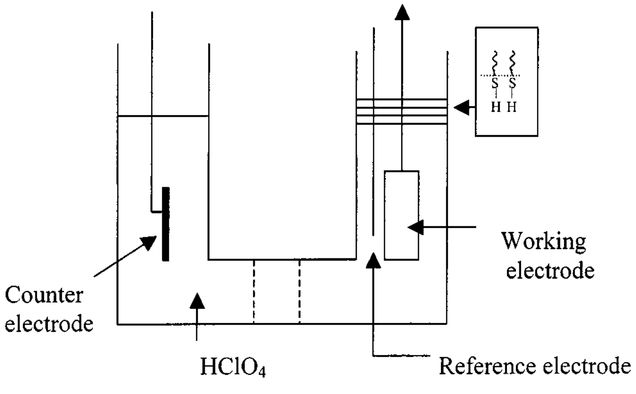


Figure 4. Electrochemical cell used by Stratmann[18]

As result of the formation of a well-ordered thiol monolayer, water does not wet this surface anymore. It has been also observed by Auger Electron Spectroscopy (AES) that an appropriate electrochemical post-treatment of the samples in neutral aqueous electrolytes significantly increases the packing density of the thiol on the iron substrate, while keeping the bond between the thiol and the metal surface intact.[26]

In view of the high reactivity of the clean iron surface either in air or in aqueous electrolytes, the high stability of this surface after modification by thiols is quite remarkable. Since this organic layer is very thin, this stability does not result from a barrier effect blocking the diffusion of oxygen and/or water. Rather, the change in the chemical and electrochemical reactivity of iron is the direct consequence of the chemisorption that saturates the clean metal surface.[27] All these results are very promising and point to the key importance of creating stable bonds between the metal and the coupling agents. These studies were, however, conducted with monofunctional molecules in order to avoid any competitive reactions of two different reactive groups of the organic molecules with the metal surface. The structure of bifunctional organic molecules now has to be optimized in order to strongly bridge metals and polymers. In this respect, the work by Itoh et al.[28] dealing with the modification of copper surfaces by bifunctional thiols is worth mentioning.

3. Electropolymerization

3.1. Brief Overview

Among the techniques suitable for the coating of metals by polymer films, electropolymerization has the advantage of proceeding through controlled reactions initiated by electron transfer to/from the monomer dissolved in the electrolytic medium. The combination of electrochemistry and polymer chemistry is far from being new and has been extensively reviewed in the last decades.[29−32] This paper does not aim at duplicating the survey of earlier works on electropolymerization, but rather at emphasizing the possible contribution of electropolymerization to the coating of metal surfaces by polymers formed in situ. Before focusing on the most relevant results obtained by Lécayon et al.[19] and our group, we will rapidly review the other contributions reported in the literature.

Wilson et al. were the first to report the electrochemical initiation of the polymerization of vinyl monomers.[33] Early works[29−33] dealt with electropolymerization occurring in solution. The formation of the initiating species results from indirect electron transfer at the electrode, i.e., by reaction of the electrolyte, followed by interaction with the monomer. These reactions are either cathodic or anodic. While free radicals are generated by the discharge of protons, peroxides or easily reducible compounds at the cathode,[33] Kolbe's reaction is the process at the anode reported most often[34] (Figure 5).

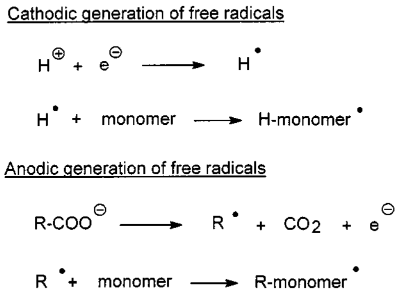


Figure 5. Polymerization initiated by free radicals[30]

Direct electron transfer from the cathode to the monomer was first suggested by Yang et al.[35] in 1957 and supported later by Funt et al.[36] Radical anions can, however, be formed by both direct and indirect processes (Figure 6).

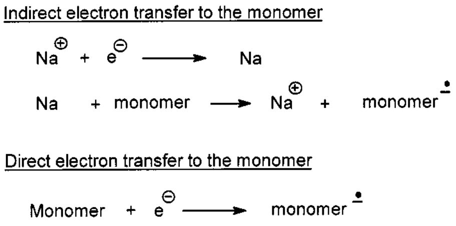


Figure 6. Polymerization initiated by radical anions[30]

According to Yamazaki et al.,[37] indirect initiation better accounts for the results reported by Funt et al. These authors proposed that direct initiation is only possible when the electrolysis is conducted under specific conditions: (i) the reduction potential of the conducting salt has to be more negative than that of the monomer, in order to avoid any indirect transfer, (ii) the electrical conductivity of the electrolytic solution must be high, and (iii) aprotic solvents have to be used in order to avoid indirect initiation by free radicals.

The deposition of polymer on the metal has been long considered as an unexpected and undesirable side-reaction, because the rapid formation of an insulating film makes the control of the process or the study of the reaction mechanism very difficult. Attempts to overcome this problem include the use of a solvent for the polymer formed, more efficient stirring and reduced electrode surface area. Lately, nevertheless, increasing attention has been paid to polymer deposition as an interesting method to protect metals against corrosion.[38−42] This coating approach is significantly different from conventional electrocoating methods that require the electrophoretic deposition of a preformed ionizable polymer from solution or suspension onto the substrate.[43−45]

Because of the high cost and potential environmental drawbacks of organic solvents, aqueous media have been extensively studied.[39] Nevertheless, Mengoli and Tidswell have investigated the cathodic electropolymerization on steel of several acrylic and methacrylic monomers in dimethylformamide and dimethyl sulfoxide.[46] The use of an organic solvent has the advantage of dissolving most organic conducting salts and of swelling most polymers of interest. Obviously, the monomer/solvent pair has to be selected in terms of poor solubility of the polymer, thus leading to film formation either by polymer precipitation or by polymer cross-linking.[47−49] The main difficulties and drawbacks met in these studies are the partial covering of the electrode, poor adhesion and poor chemical stability.

Since 1980, an increasing number of interesting papers have been published on this topic,[50] particularly on the synthesis of polymer composites containing carbon fibers[51] and on the coating of metal surfaces for aerospatial or electronic applications.[52] Undoubtedly as soon as new techniques dedicated to the design of stable polymer−metal associations are available, new application fields will develop rapidly. In this respect, the contribution of Lécayon et al., reviewed in ref.[19], is of major importance.

3.2. Electrografting of Organic Polymers onto Common Metals

Lécayon et al. have demonstrated that electrochemistry is well suited to the building up of an adherent insulating polyacrylonitrile (PAN) film onto the surface of common metals.[19,53,54] They have studied the cathodic electropolymerization of acrylonitrile (AN) in rigorously anhydrous acetonitrile (ACN), containing tetraethylammonium perchlorate (TEAP) as a conducting salt. In the case of the acrylonitrile (AN)/nickel system, the mechanism proposed for the surface modification is sketched in Figure 7. The negative polarization of the nickel electrode has three major effects: (i) the formation of the cathode double layer, (ii) the reduction of the metal oxide layer, and (iii) the formation of an electron-rich metal surface, which can act as a base. As a result of the electric field at the cathode and the strong dipole moment of AN (3.9 D[55]), the acidic vinyl β-carbon atom of acrylonitrile is orientated towards the metal. A Lewis acid−base reaction can then occur, leading to strong bonding between AN and Ni (chemisorption). According to the authors, the π electron doublet referring to the original vinyl bond of AN is transferred to the substituted carbon atom (CH), so that the basic character originally located at the surface of the electrode is displaced to the end of the first attached AN molecule. Monomer addition can then be repeated many times, which leads to the formation of a strongly bonded PAN film. The PAN film and the PAN/metal interface have been investigated by a number of spectroscopic techniques:[56−60] XPS, IR, ellipsometry, ultraviolet photoemission spectroscopy (UPS), electron-induced X-ray emission spectroscopy (EXES). Electrochemical impedance data[60] show that the metal surface is more efficiently blocked by electrodeposited PAN than by PAN merely cast from solution. The direct observation of C−Ni bonds formed at the interface has also been reported.[59]

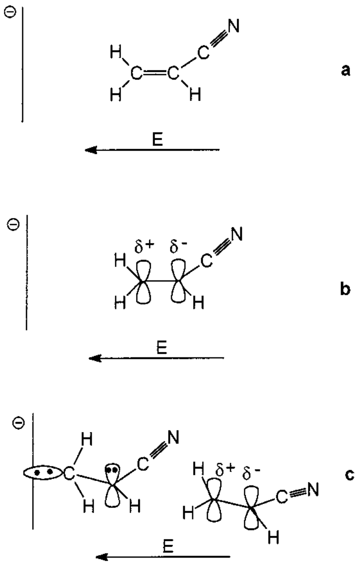


Figure 7. Molecular model for the acrylonitrile/metal interaction in the cathode double layer according to Lécayon et al.:[54] a) the molecule is oriented; b) the molecule is polarized; c) a chemisorbed radical anion is formed, which can interact with another molecule; polymerization then propagates by means of an anionic mechanism

The "grafting" reaction reported by Lécayon et al. differs from previous studies [61−63] that showed the formation of AN radical anions, followed by rapid dimerization and anionic polymerization initiated in solution by both anionic ends of the species. It is worth noting that the two peaks in the voltammogram recorded during AN reduction (Figure 8) were never observed before. According to Viel,[64] the two reduction peaks stem from surface passivation (less cathodic peak, referred to as peak I) and from a diffusion-controlled process (peak II), respectively.

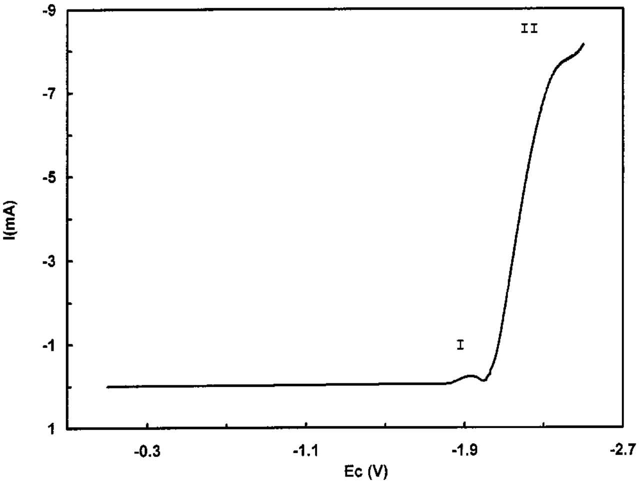


Figure 8. Cathodic response of a 0.1 M AN solution in acetonitrile; [TEAP] = $5 \cdot 10^{-2}$ M, v = 20 mV·s^{-1}

In addition to the so-called grafted polymer, this author also mentions the formation of non-grafted chains[64] which are easily removed by rinsing the electrode with a solvent for PAN, such as dimethylformamide (DMF). It is also proposed that the "grafting reaction" is likely to occur at potentials less cathodic than peak II, but no clear experimental information is provided about the formation of non-grafted chains. Originally, the grafting reaction, i.e., the chemisorption of AN radical anions, was described as a "secondary electrode reaction",[65] when compared to dimerization and polymerization occurring in solution.[63] In fact, the grafting reaction has been observed thanks to the rigorous experimental conditions used by Lécayon et al.[66]

3.2.1. Experimental Requirements

Contamination of the metal surface by oxide and any organic impurities is detrimental to strong monomer chemisorption. Thus, careful cleaning of the electrode substrate is a prerequisite to impart stability to the interface between the metal and the organic molecule, as confirmed by Stratmann et al.[18] The whole grafting reaction must thus be conducted in a glove box under dry and inert conditions. The nickel oxide is reduced in the electrochemical cell filled with a solution of the monomer and the conducting salt at potentials less cathodic than the potential required for the AN reduction (Figure 9).

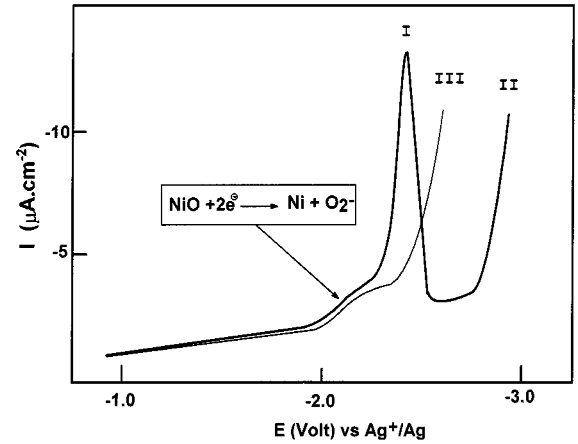


Figure 9. Voltammograms in ACN/TEAP solutions: I and II are the inhibition peak and the diffusion peak, respectively, when the solution contains AN; III in absence of AN[54]

Ellipsometric measurements have been carried out in situ during the first step of the cathodic electropolymerization of acrylonitrile on nickel, and they have confirmed that the grafting reaction is initiated at the electrode sites released by the reduction of the native oxide.[58] This observation explains why grafting is usually observed on metals such as Ni, Fe, or Cu, whereas it does not occur on metals for which the oxide cannot be reduced electrochemically (e.g. Al, Zn).[67−69]

The use of a conducting salt which is inert in the potential range in which the electrochemical signature of the AN electroreduction is observed has to be pointed out. Indeed, according to Yamazaki et al.,[37] inorganic conducting salts such as $NaNO_3$, are commonly reduced at potentials less cathodic than the monomer, leading to the indirect initiation of the polymerization in solution (Figure 6). In a patent,[66] Lécayon et al. recommend the use of tetraethylammonium perchlorate (TEAP), which is known for its electrochemical stability up to high cathodic potentials.[70]

The purity of solvents and monomer has also a critical importance for the grafting reaction to be successfully achieved. According to Lécayon et al.,[67] impurities, such as H_2O and O_2, can slow down or inhibit the polymer deposition. Their content in the electrochemical solution has to be lower than 5−10 ppm. These features have been confirmed by Mertens[68] who deliberately contaminated the electrochemical solution by increasing amounts of water or oxygen. The main effect of small quantities of water added to the ACN/TEAP solution is to shift the upper limit of the cathodic window (current rise attributed to the solvent reduction) towards less cathodic values and to increase the intensity of peak I (Ip_1, Table 1).[68]

Table 1. Peak *I* intensity [μA] with increasing water amount, [AN] = 1 M; ACN/TEAP; v = 20 mV·s^{-1}

Water content [ppm]	Ip_1 on Ni [μA]	Ip_1 on steel [μA]
10	30	30
100	125	80
400	200	−

According to Viel,[64] the intensity of peak I is strongly dependent on the polymerization kinetics, the inhibition time being controlled by the rate of formation of the insulating polymer film.

The increase in the intensity of peak I thus indicates a slower inhibition of the cathode. An explanation might be the earlier termination of the grafted chains by water, consistent with formation of thinner films as measured by ellipsometry (ex situ measurements).[71] When the water content is increased further, non-bonded chains are predominantly formed as a result of indirect initiation by hydrogen radicals (Figure 5). The film adhesion is rapidly lost, since it is composed mainly of non-bonded polymer chains embedded in a few grafted ones.

In contrast to water, the reduction of oxygen ($O_2 + e^- \rightarrow O_2^-$) dissolved in the electrochemical medium gives rise to a well-defined voltammetric wave at potentials less cathodic than the AN reduction. In that case, according to Mertens, the indirect initiation of the AN polymerization by the reduction by-product is the predominant process, at the expense of the grafting reaction.[68]

3.2.2. Recent Advances

Owing to the interest and potential of this unusual electrografting reaction, Mertens et al. recently reinvestigated[68,72−73] the cathodic reduction of acrylonitrile (AN). In the opinion of those authors, the intimate mechanism of the AN electropolymerization was still unclear. This is the reason why they studied this electrochemical reaction in acetonitrile (ACN), a poor solvent for PAN commonly used by Lécayon et al., as well as in dimethylformamide (DMF), a good solvent for the polymer.

Mertens et al. used mechanically polished metal plates as working electrodes, instead of polycrystalline substrates prepared by sputtering a thin layer of pure Ni onto polished metal plates under high vacuum.[67] The surface oxide of the electrode was electrochemically reduced in an ACN/TEAP solution in a glove box just prior to polymer deposition from a fresh solution of monomer. This two-step process prevents O_2^- species from being formed in the monomer solution, thus avoiding possible cross-linking of PAN.[68]

Mertens et al.[72][73] pointed out the critical role of the applied potential, showing that PAN is strongly bonded to the nickel cathode only at the potential of peak I (Figure 8). In this potential range, a thin homogeneous and colorless polymer film is formed, even when the reaction is conducted in a good solvent for PAN, such as dry DMF. This observation confirms the strong adhesion of the PAN film onto the cathode, consistently with the grafting claimed by Lécayon et al.[53] In sharp contrast, a PAN film spin-coated onto nickel is rapidly dissolved in this solvent. When the potential is further increased (Figure 8, peak II), no grafting is observed anymore; the polymerization then proceeds in solution. These non-grafted chains are rapidly dissolved in DMF, while they are merely precipitated on the cathode as a thick yellowish non-adherent film in ACN. Although PAN films formed at the potential of peak I are generally too thin and too smooth to be visible by scanning electron microscopy (SEM), Figure 10 shows the nucleation of the PAN chains formed at the potential of peak II in ACN, leading to a cauliflower-like morphology.

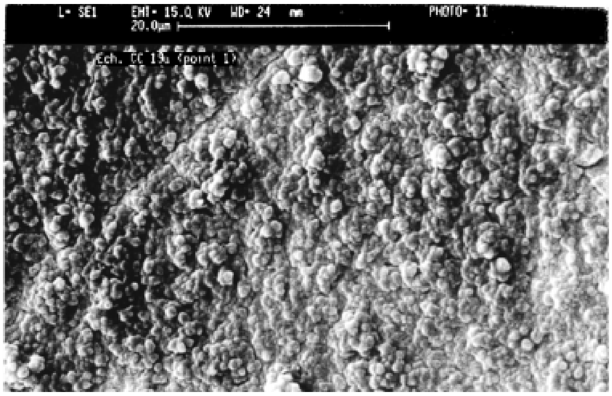


Figure 10. Scanning electron micrograph of PAN film deposited on Ni in a 0.05 M TEAP solution in ACN at the potential of peak II[68]

Mertens et al.[74] investigated the identification of the species responsible for the polymer propagation and tentatively proposed two different mechanisms for the AN electropolymerization in relation to the applied potential. The reaction that occurs at the potential of peak I does not fit classical electrochemical models since the intensity of peak I decreases when the monomer concentration increases; the process seems to be neither fully faradaic nor fully capacitive in nature. In order to identify the species active at the two reduction potentials, agents able to react selectively with radicals or anions and inert in the potential range of interest were added to the electrolyte solution. The addition of either diphenylpicrylhydrazyl (DPPH), radical scavenger or ε-caprolactone (probe for anionic polymerization) led to evidence for the formation of a radical species that initiates and propagates the PAN firmly attached to the Ni cathode (Figure 11).

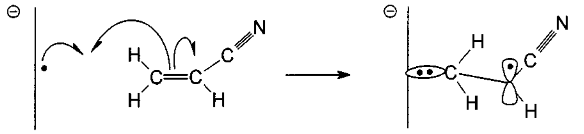


Figure 11. Mechanism proposed by Mertens et al. for the AN grafting reaction at peak I[74]

At the more cathodic potential (peak II), reduction of AN is a faradic process based on the transfer of one electron to the monomer, and on the formation of a radical-anion that rapidly dimerizes and initiates the AN polymerization in solution, in agreement with previous work by Bhadani et al.[63] In addition to this dual mechanism, a possible bond-breaking of the originally "grafted" PAN chains has to be considered when the potential becomes more cathodic than that of peak I.[74] In ACN, an increasingly more cathodic potential is also responsible for the strain of the originally grafted film, so that the conductivity of the cathode is restored locally, allowing the anionic polymerization of AN to occur and to lead to PAN films with a cauliflower aspect (Figure 10).

The model proposed by Mertens et al. (Figure 11) differs markedly from that of Lécayon et al. (Figure 7), who proposed an anionic mechanism for the grafted growing chains. Nowadays, the electrografting mechanism is still a matter of controversy.[75] Whatever the structure of the propagating species, the most important result is the clear identification of the potential range in which the formation of an adherent polymer film can be controlled. In this respect, dynamic mechanical thermal (DMTA) and infrared spectroscopic analyses[76] have recently shown that the structure of the PAN film depends on the potential at which it is formed. Indeed PAN "grafted" at the potential of peak I is mainly isotactic and the film is amorphous, in contrast to ungrafted PAN formed at more cathodic potentials, which is mainly atactic and forms a paracrystalline film in ACN.

In order to control the film thickness and roughness, these features have been studied in relation to the solvent used and the monomer concentration. The thickness of dried films prepared in the potential range of peak I was measured by ellipsometry; it clearly depends on these experimental parameters[72] (Figure 12). The film was thicker in DMF than in ACN and this can be rationalized on the basis of the precipitation of the growing PAN chains in the latter case and the solvation of the chains in the former case. Indeed, as soon as the PAN chains reach some critical length in ACN, they precipitate on the electrode, which is detrimental to their propagation. The situation is completely different in DMF, since the growing chains are solvated during the whole polymerization.

This qualitative explanation is supported by Atomic Force Microscopy (AFM) data which show that PAN films deposited in DMF at high monomer concentration are thick enough to mask the morphological features of the substrate. Figure 13 is a typical image of the bare nickel surface which is used as a reference for the observation of the coated electrodes. Generally, the morphology of thin PAN films, grafted in ACN or DMF at low AN concentration (0.1−0.2 M), appears to consist of small polymer grains deposited on the electrode (Figure 14, A and 14, B). The average size of the grains is in the 40−60 nm range over the whole surface. The polymer deposit is not thick enough to mask the largest defects of the nickel surface (as ridges present on Figure 13 are still visible on Figure 14, A and B). At higher AN concentrations (1−2 M), clear morphological differences are observed depending on the solvent used (Figure 15, A and B). Films prepared in ACN show the same granular morphology as in dilute solution, with characteristic sizes of approximately 50 nm (Figure 15, A). However, the ridges of the original metal surface are less visible, in agreement with the formation of thicker films. Details reminiscent of the metal surface are no longer ob-

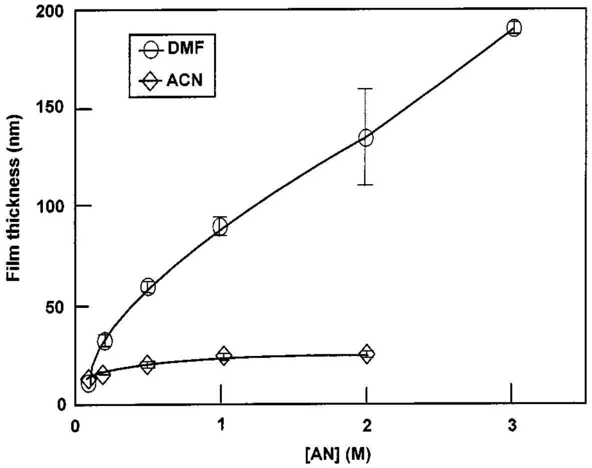


Figure 12. Dependence of the PAN film thickness on the monomer concentration in ACN and DMF[72]

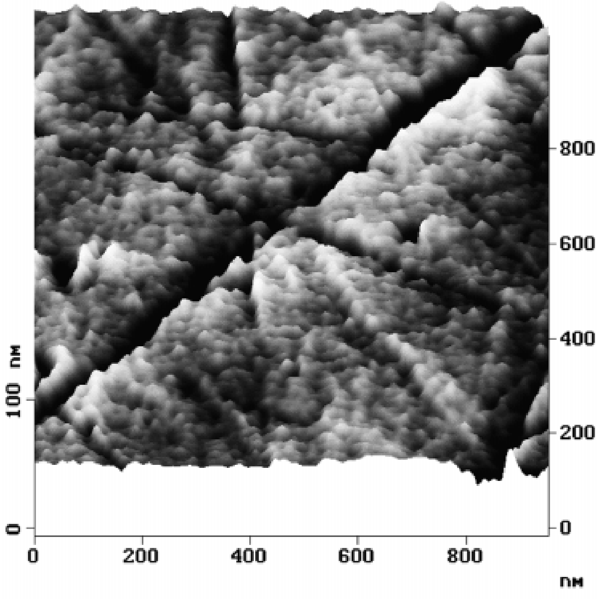


Figure 13. Atomic force micrograph of bare nickel

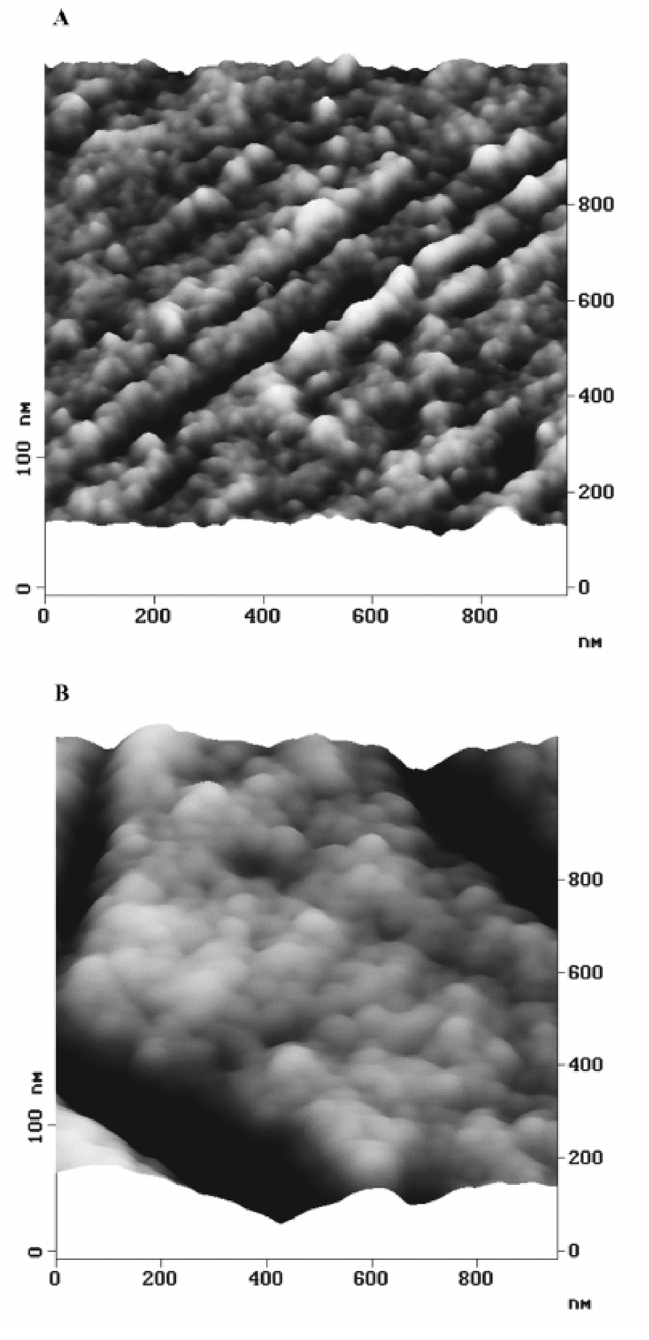


Figure 14. Atomic force micrographs of PAN films deposited on Ni in the potential range of peak I: A) AN 0.1 м in ACN; B) AN 0.2 м in DMF

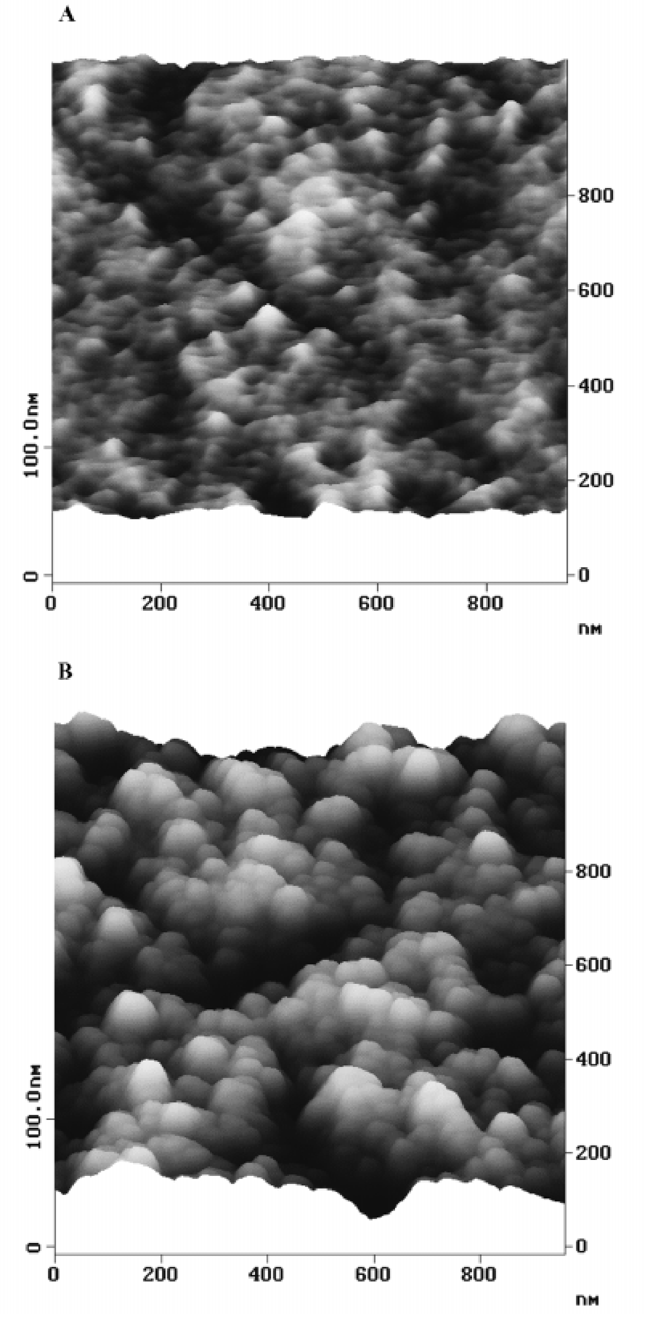


Figure 15. Atomic force micrographs of PAN films deposited on Ni in the potential range of peak I: A) AN 1 м in ACN; B) AN 2 м in DMF

served in films grafted in DMF (Figure 15, B). In this case, the PAN deposit is clearly thicker and the film consists of nodules much larger in size (100 to 150 nm) than the grains observed in ACN.

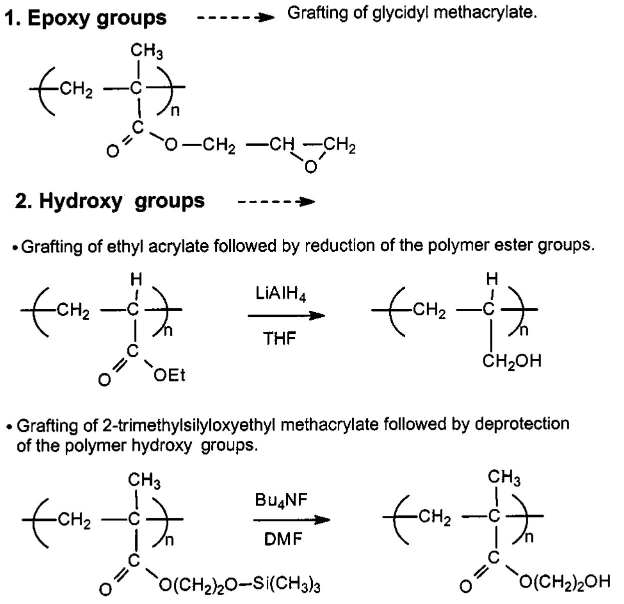
As direct applications of the fine control of the AN electrografting, specific achievements have been reported, for example, preparation of thin α-emitting sources by simultaneous electroreduction of AN and uranium salts,[77] preparation of electrical connectors by an adequate thermal post-treatment of electrografted PAN thin films[78] and protection of art pieces.[68,79]

Very recently, efforts have been devoted to improve the understanding of the electrografting reaction and to functionalize the very adherent thin films formed. The unusual electrografting reaction has been shown to strongly depend on the ability of the monomer to be adsorbed onto the clean cathode. Therefore, the monomer has to compete efficiently with the solvent and with the conducting salt[80] to be adsorbed and react at the cathode surface rather than in solution. ^{13}C NMR spectroscopic data and theoretical calculations[81] have shown that AN is particularly prone to interact strongly with the cathode. Nevertheless, paying special attention to the competitive adsorption of monomer and solvent (or conducting salt), (meth)acrylic monomers have been successfully grafted.[80,82]

Furthermore, the use of coupled quartz crystal microbalance and cyclic voltammetry has confirmed that the inhibition peak is the actual signature of the strong monomer chemisorption and growth of grafted chains.[82] At more cathodic potentials, polymerization occurs in solution, while previously bonded chains are detached from the electrode. In this respect, a major difference has been pointed out in the behavior of acrylic and methacrylic monomers. Indeed, in the latter case, bonded and non-bonded chains are simultaneously formed in the potential range of peak I. Acrylic polymers are thus better candidates for the efficient coating and long-term protection of metals.

The possibility of electrografting acrylonitrile-containing copolymers has also been investigated.[83] As a rule, the composition of the grafted chains depends on the local concentration of the comonomer. If the comonomer has no tendency to accumulate in the close vicinity of the cathode (e.g. vinyl acetate), then only homopolyacrylonitrile is grafted. In the reverse case (e.g. ethyl acrylate), copolymer chains are grafted, and the composition of the film depends mainly on the capability of each comonomer to compete with the solvent for adsorption. However, the capacity of the films to cover the electrode seems limited, possibly as consequence of the extra competition of the two monomers to adsorb onto the cathode. In order to alleviate this disappointing situation, the sequential electrografting of each monomer in two different cells has been proposed.[84] Mixed films, combining the properties of two polymers, are formed when the monomer less prone to compete with the solvent molecules is electrografted first at a more cathodic potential than the second monomer. Since the grafting density is expected to depend on the adsorption of the monomer, this result supports the general idea of the competitive monomer/solvent adsorption onto the cathode in the very first step of the grafting process. In the same way, the full electrochemical synthesis of insulating/conducting composites has also been investigated.[85] An unexpected application has also been found by using electrografted substrates as templates for the synthesis of conducting polymers leading to formation of polypyrrole wires.[86]

The electrografting technique thus allows for the control not only of the adherence of organic coatings on metals, but also of their nature and composition. For example, it is now possible to prepare electrografted films containing epoxy groups in one step, and films containing hydroxy groups in two steps (Scheme 1).[87] In this respect, it is worth noting that the electrografting of 2-hydroxyethyl methacrylate (Scheme 1) could pave the way for biomedical applications (e.g., catheters).



Scheme 1. Functionalization of electrografted films

4. Conclusions and Challenges

The electrochemical strategies proposed by Stratmann et al.[18] and Lécayon et al.[19] have brought valuable answers to the problems caused by the weakness and short lifetimes of polymer−metal associations. From an economic point of view, the approach by Stratmann et al. is more advantageous, since it can be carried out under mild conditions in water, in contrast to the electrografting proposed by Lécayon et al. Extension of the model systems studied by Stratmann et al. to real systems consisting of the adsorption of bifunctional organic molecules and the reaction of the modified surface with film-forming monomers in the next turning point to pass.

Despite some stringent experimental conditions, electrografting appears to have a promising future for the preparation and protection of small-size and high-value devices.[77−79] One pending problem is the small thickness of the grafted films. Indeed, a polymer coating usually imparts corrosion resistance to a substrate when the thickness is greater than 50µm.[88] At present, the electrografted films do not provide this beneficial effect since the number of deposition cycles and the deposition techniques (voltamperometry, chronoamperometry, chronopotentiometry) do not allow for an increase in the final thickness of the film.[72]

The use of the grafted coating as a primer also becomes more promising with the ability to graft a larger number of monomers.[80−82,87,89−92] In this field, the controlled chemical modification of grafted films remains a challenging issue. The copolymerization of AN with "functional" monomers such as acrylate, and the electrografting of blends could be an interesting way to combine various interesting properties at the surface. Recent developments resulting in the diversification of the grafted substrate allow for the preparation of primers able to interact strongly with a top-coat.

The search for new monomers prone to electrografting remains the best way to simultaneously overcome the two main drawbacks of the polymer−metal association; i.e., the weakness of both the substrate/polymer and polymer/surrounding medium interfaces.

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