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A METAL-POLYMER INTERFACE STUDY USING ELECTROPOLYMERIZED ACRYLONITRILE ON NICKEL SURFACES

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ABSTRACT

Studies of the interface between mineral and organic materials have been realized for a couple formed between pure transition metal and a polar and polarizable molecule (acrylonitrile).

The results presented show the effects of a local electric field on the activation processes associated with adsorption sites and the molecule, interaction mechanisms and the resulting types of chemical bond.

The structural, electronic and chemical properties of a nickel-polyacrylonitrile interface are described.

Molecular and energetic qualitative models for the interaction mechanisms are proposed.

KEY WORDS: Adhesion, Polymer-metal interface, Polyacrylonitrile, Bonding mechanism, Polymerization mechanism, Surface reactivity, Acid-base reactions.

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INTRODUCTION

Many of the problems often classified under the very general category of "materials science" involve interactions between organic and mineral materials ; many examples can be cited, for example gluing, realizing adherent coatings, or lubrication under non-hydrodynamic conditions. In all cases, accurate studies of the interface should be carried out on the materials developed in addition to bulk wear studies. Investigations should relate to:

- the nature of the interface (i.e. whether the bond is mechanical, physical or chemical and how it has been realized),
- the spatial properties of the interface based on both chemical considerations (i.e. whether there is any interpenetration of one material into the other) and physical considerations (i.e. whether the presence of one of the partners has any effect on the properties of the other),
- the wear properties of the surface (i.e. spontaneous aging or stress aging).

Very significant questions are therefore posed. Such questions should be handled from different but complementary points of view.

The purpose of the present work is to contribute towards a better understanding of molecular level processes related to interactions between mineral and organic materials. In order to realize this objective we studied more accurately the interaction between acrylonitrile (AN) molecule (CH_2CHCN) and metal surfaces leading to the grafting of a polyacrylonitrile (PAN) film /7/. This system is indeed simple enough to allow a detailed interpretation of the results obtained and modeling the phenomenon observed. The system studied is, however, sufficiently realistic to be representa-

tive of the technological problems encountered in practice:

- the mineral material considered is a pure polycrystal transition metal with an optically flat surface (polished),
- the organic material considered is a polarizable, polymerizable polar molecule (acrylonitrile: $H_2C = CH-C \equiv N$),
- at the time when the interface is formed the surrounding environment is either an ultra-high vacuum (residual pressure of less than 10^{-8} Pa) /11/, or an electrically conducting organic solution (acetonitrile and tetraethyl ammonium perchlorate) maintained in an argon atmosphere /2/.

The first part of this paper is devoted to studies of the mechanisms involved in the construction of the interface ; we will report successively on the behaviour of the interacting organic molecule and on the evolution of the surface electronic states of the metal surface. In the second part, we will deduce from the obtained results a molecular and energetic model of the interactions in the case of the solid-liquid negatively polarized interface.

INTERACTION MECHANISMS BETWEEN ORGANIC MOLECULES AND METALS

An ordinary solid, even metallic (pure metal or alloy) always exhibits surface heterogeneities leading to surface properties. These heterogeneities are related to the presence of ionic or covalent (oxide, carbide, etc) surface layers characterized by stoichiometric defects, inhomogeneities, impurities and defects in crystal structure (distortion, steps, dislocations). As a result, the surface potential (which for a perfect metallic single crystal is very smooth) becomes extremely tortuous ; the abruptly changing surface induces intense electric fields strongly localized about defects; these fields significantly affect the reactivity of the surfaces involved:

- by activating surface reactive sites (dangling bonds, out-of-equilibrium atoms) through modifications to their electron affinities thereby intensifying donor (basic) or acceptor characteristics ;
- by their effects on molecules in contact with the surface, principally polar and polarizable molecules, a typical example being multiple bond functionalized organic molecules. Orientation orbital degeneracy phenomena will thus develop and contribute towards activating surface interactions by enhancing acid-base type reaction mechanisms.

Since the electric field localized at the surface plays a decisive part, electrochemical electrodes are well suited tools to initiate such an electric field. Indeed the electric field located in the electrochemical double layer is very intense /10/. According to the polarization of the electrode, the metal surface becomes a system of electron acceptor sites (anode) or of electron donor sites (cathode), and its expected behaviour will thus drastically change.

This is clearly pointed out with our results obtained either with a negatively polarized surface (cathode), or with a positively polarized surface (anode), or with a non-polarized surface.

BEHAVIOUR OF THE INTERACTING ORGANIC MOLECULE

Negatively polarized metallic surfaces

In this case, the negatively polarized sample (cathode of an electrochemical cell) is immersed in an organic liquid and transforms into an ensemble of electron donor sites.

The formation of a cathodic double layer on the application of a negative potential is schematically shown in fig. 1a. The molecule is orientated by the electric field through an interaction with its dipolar moment localized along the nitrile $-C \equiv N$ group. Moreover the vinylic bond $>C=C<$ is polarized by the electric field as well as by the inductive effect of the nitrile group. So the CH_2 end of the molecule becomes slightly positive and behaves as a so called Lewis acid. It can interact with the basic sites induced at the metal surface by the cathodic polarization. This acid-base reaction is responsible for the bonding of the molecule on the surface. The same type of reaction between the first adsorbed molecule acting now as a base and another activated molecule lead to the polymerization. It successively reproduces itself over the subsequently modified surface and finally results in the formation of a polymer film.

With the aid of Metastable De-excitation Spectroscopy (MDS: fig. 1b) as well as ab initio calculation of the ionization potentials of the AN molecule /12/, we showed that the film surface consists essentially of electronic lone pair orbitals from nitrogen atoms attached to terminal nitrile groups. So the last $-C \equiv N$ groups are oriented towards the outer surface of the film as expected from the electric field influence. This result has been confirmed by Infrared Reflection Absorption Spectroscopy (IRAS) using a polarized light beam: the $-C \equiv N$ groups have the same orientation in the whole film. Finally, all these results

lead to the molecular structure schematized in fig. 1c for the resulting polymer-film.

Because of the technological usefulness of this situation (production of a polyacrylonitrile film strongly adhering to metal /7/, the major part of our work has been devoted to the corresponding experimental research and the modeling of this phenomenon /3,4,8,9,13,14,15,16/.

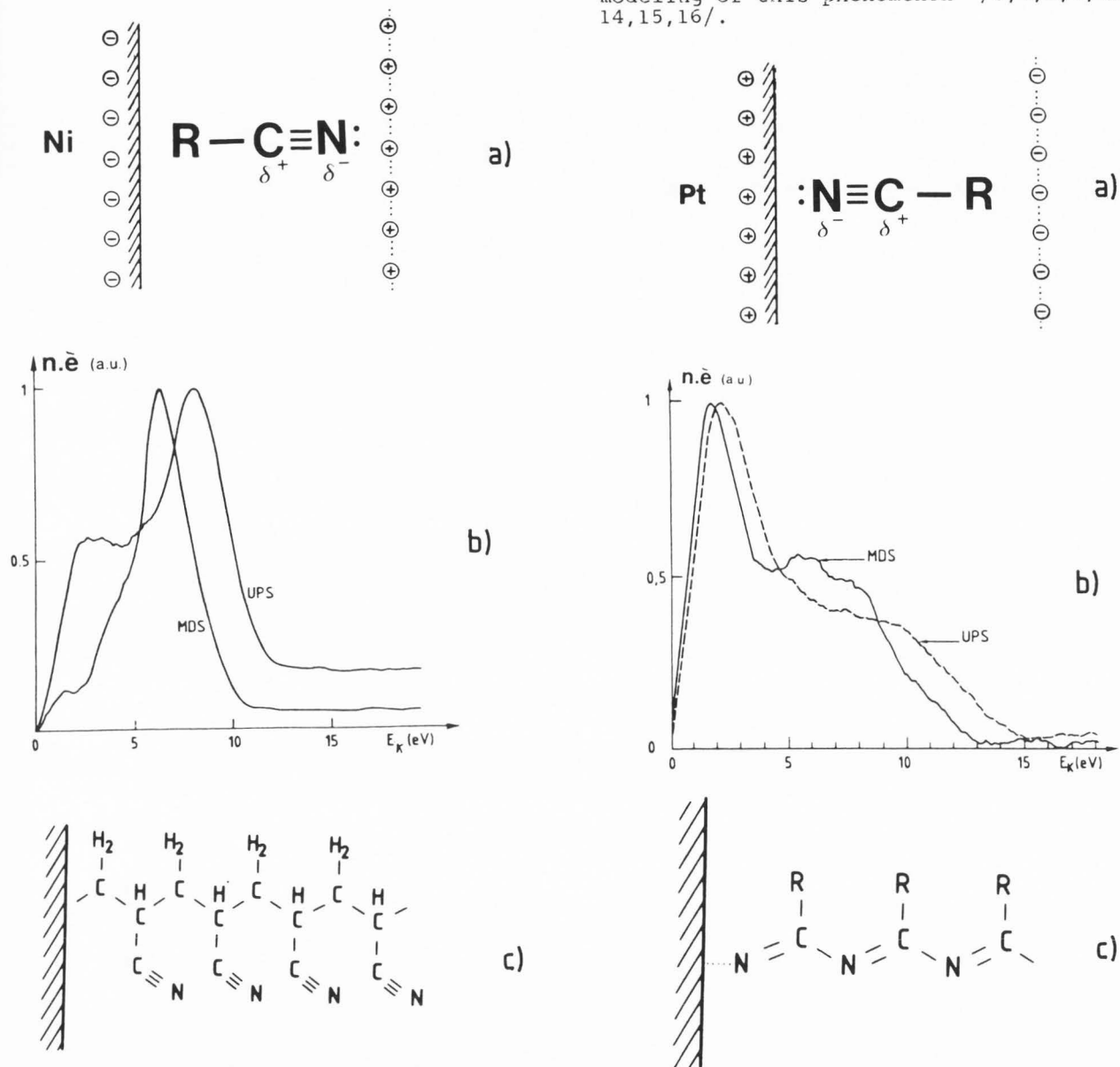


Fig. 1. Negatively polarized surface.
 a) electrostatic image of the interaction: the molecule is situated in the cathodic double layer.
 b) MDS and UPS studies of the modified surface.
 c) molecular image of the obtained polymer (deduced from IRAS measurements).

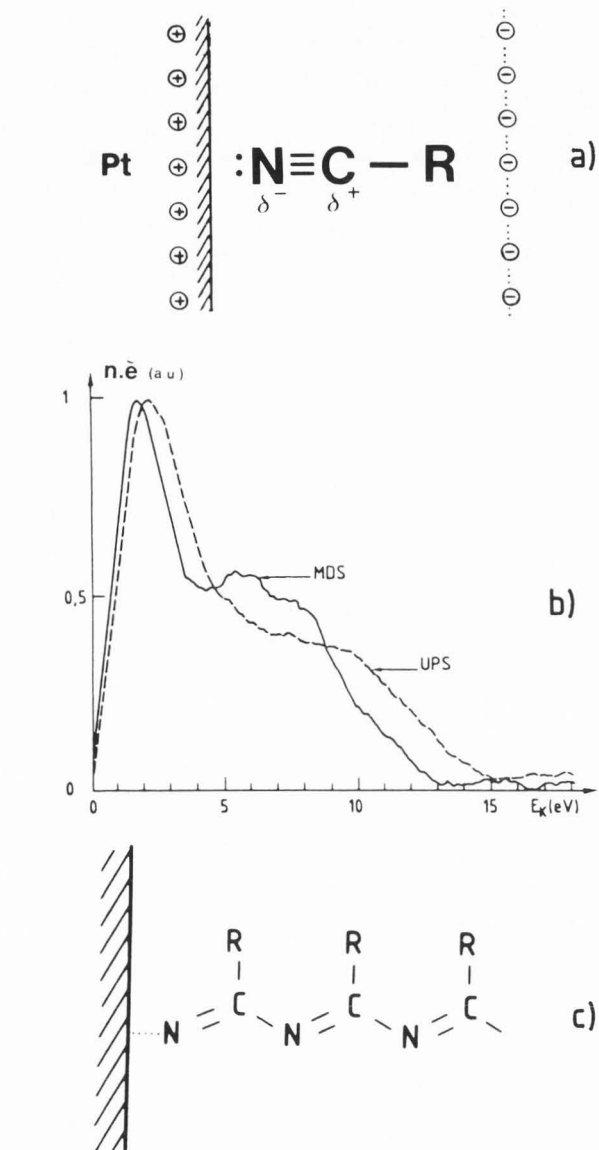


Fig. 2. Positively polarized surface.
 a) electrostatic image of the interaction: the molecule is situated in the anodic double layer.
 b) molecular structure of the obtained polymer (deduced from IRAS measurements).
 c) MDS and UPS studies of the modified surface.

Positively polarized metallic surfaces

A sample immersed in an organic solution and positively polarized serves as an anode. Because of its polarization, the surface is therefore an electron acceptor and of an acid nature. In order to avoid surface modifications through oxidation, platinum is used. The formation of an anodic double layer on the application of a positive potential is shown very schematically in figure 2. The molecule presents now its basic end (i.e. electron donor) to the electrode surface when oriented by the electric field (fig. 2a). The resulting organic molecule-metal bonding and the formation of a polymer film can also be explained in terms of an acid-base reaction model. A simplified structure (fig. 2b) is deduced for this film from infrared reflection absorption spectra.

The electronic properties of the outside face of the film are determined by photo-electron spectroscopy (UPS) and metastable de-excitation spectroscopy (MDS) /1/ shown in figure 2c. It appears that these spectra are very different from those recorded in the case of the cathodic interaction (fig. 1b) and are coherent with the conjugated molecular structure presented in fig. 2b: absence of the nitrogen lone pair orbital and broadness of the electron emission band. It is emphasized that anode polymerization reactions are probably induced not only by the double layer electric field, but also by negative ions and impurities found as dopants in the resulting material, which consequently possesses a complex structure. Several authors who studied similar systems suggest such reactions /17/.

Non polarized metal surfaces

In this case, the sample possesses a metallic surface which is clean at the "atomic level" (polycrystalline nickel cleaned using classical physicochemical procedures for surfaces). It is exposed at room temperature to 100 Langmuirs of acrylonitrile in the vapor phase. The experiment was performed using a conventional ultra-high vacuum facility (residual pressure less than 10^{-8} Pa) and surface changes monitored by UPS and MDS /11/. Under these conditions, the organic molecule-surface reaction depends on the intrinsic properties of the two partners: the nature of this surface can be deduced from the experimental results (fig. 3).

A comparison of the photo-electron spectra (fig. 3a) before and after exposure to a rarefied acrylonitrile atmosphere ($P \sim 10^{-5}$ Pa) suggests that an adsorbed layer is formed: diminished signal corresponding to the 3d nickel band, observation of a band of

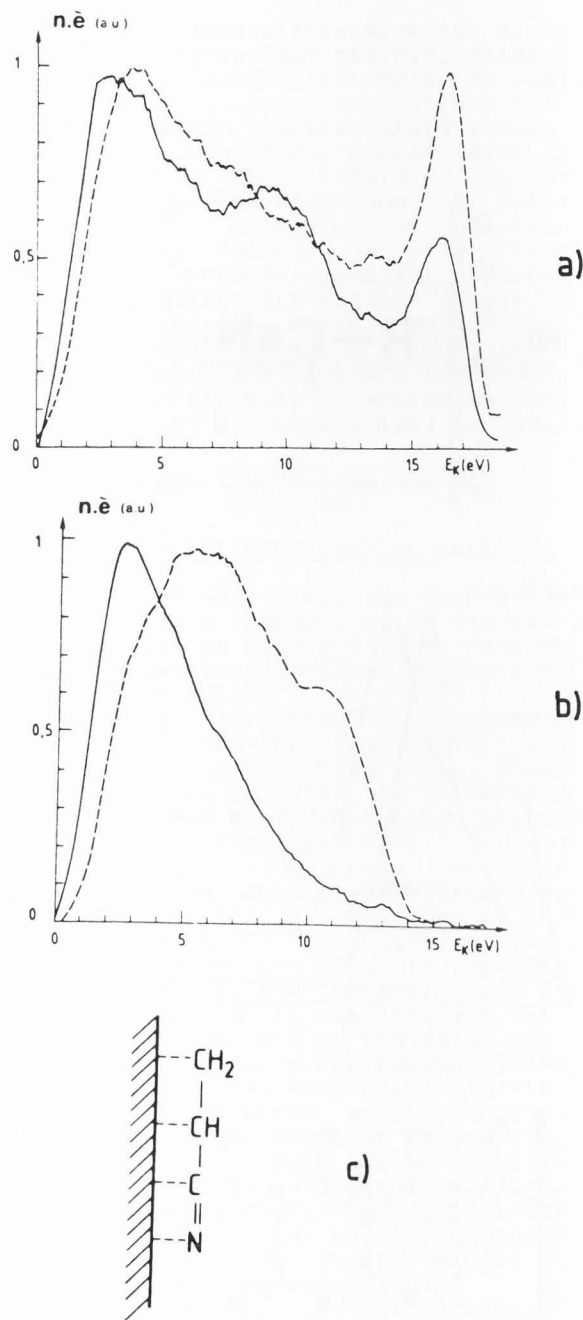


Fig. 3. Non polarized surface.

- a) UPS study of the chemisorption of acrylonitrile molecules onto nickel (---: clean nickel; —: nickel exposed to acrylonitrile).
 b) MDS study of the chemisorption of acrylonitrile molecules onto nickel (---: clean nickel; —; nickel exposed to acrylonitrile).
 c) Model for the acrylonitrile adsorption onto nickel.

occupied levels at between -5 and -10 eV beneath the Fermi Level. The transparency

of this layer to photo-electrons from the metallic substrate nevertheless suggests that it is less than 1 nm thick.

In the MDS case (fig. 3b), the electron emission band located at about $E_k = 12$ eV disappears almost completely after the acrylonitrile adsorption without the emergence of any emission band characteristic of the molecule. The 12 eV band is the self-convolution product of the nickel 3d band due to the de-excitation mechanism of the metastable atom in front of a metal surface: Resonant Ionization + Auger Neutralization /5/. The shape of the MDS spectrum after adsorption indicates a permanence of the RI + AN mechanism in spite of the surface coverage by the acrylonitrile molecules. From this observation, we can deduce that the molecule lies flat on the surface as schematized in figure 3c. This is in good agreement with other works dealing with the chemisorption of CH_3CN on a polycrystalline nickel surface /6/. In this case, the π orbitals of both vinylic bond and CN group are involved in the bonding with the surface; it is not possible for polymerization phenomena to result from such a situation.

EVOLUTION OF THE SURFACE ELECTRONIC STATES

In the preceding section, we pointed out the influence of the electric field on the molecular behaviour, and we have assumed the creation of electron donor or acceptor sites. We now will discuss the nature of these sites and how they are created in the case of oxidizable metals. This will be shown for a nickel cathode. The evolution of the surface electronic states are studied either by associating ionic abrasion and Auger electron spectroscopy (Auger profiles) or by associating UPS and MDS on films with a thickness less than the mean free path of the photoelectrons. Auger profiles enable the chemical composition of the metal-film interface to be characterized (fig. 4). The spectrum (a) was obtained from the nickel surface before electrochemical treatment. The sample surface is contaminated (oxygen O and carbon C). The spectrum (b) was obtained after depositing a PAN film by cathodic electrochemical treatment: only PAN constituents are seen. Spectra c, d and e were obtained after ionic abrasion for increasing times. The spectrum c corresponds to the time necessary to reach the interface as seen by the emergence of the nickel Auger lines. Further controlled abrasions (spectra d and e) produce the disappearance of the nitrogen Auger line, but the oxygen initial line does not appear again. The simple presence of lines characteristic of carbon and nickel

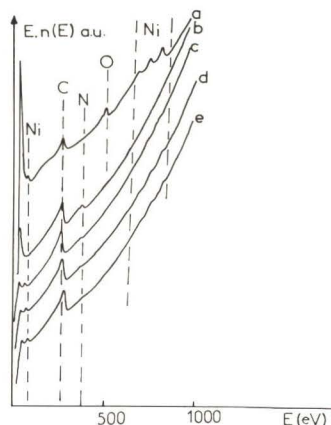


Fig. 4. Auger profiles of the PAN-Ni system ($E_p = 2.5$ keV, $i_p = 5 \cdot 10^{-9}$ A).

- initial surface (polycrystalline nickel exposed to atmosphere).
- electrochemically treated surface (organic film coating), and exposed to atmosphere.
- surface b submitted to an ionic abrasion (20 mn, Ar^+ , $E_p = 1$ keV, $i_p = 10^{-6}$ A).
- surface c + 3 mn of ionic abrasion.
- surface d + 3 mn of ionic abrasion: disappearing of the organic film, absence of the oxygen Auger line.

in the spectrum shows the pre-existing oxygen of the sample has been completely eliminated in the electrolytic cell by reduction process and no new contamination has appeared: all the available chemisorption sites have been occupied by AN as soon as they were liberated by oxygen.

The Ni-PAN interface was then studied simultaneously by UPS and MDS using samples obtained by low cathodic potential electrochemical treatment in such a way as to ensure a film thickness of less than the mean free-path of the photoelectrons ($\lambda \sim 1$ nm): the lengths of the polymer chains then correspond to only a few monomer units. The comparison of the UPS spectrum recorded before and after the electrochemical treatment (fig. 5) confirms the results obtained by AES: the UPS spectrum after treatment shows the decrease of the oxygen 2p band at 5.5 eV, the increase of the Ni 3d band and the appearance of the band characteristic of the PAN (see fig. 1b).

All the results reported in the present section show that the polymer grafting at the cathode needs the reduction of the oxide initially present on

the surface and originates in a chemisorption reaction between the valence electronic states of the metal and the molecular site selected and activated by the electric field. We are now able to propose a model of the interaction mechanism.

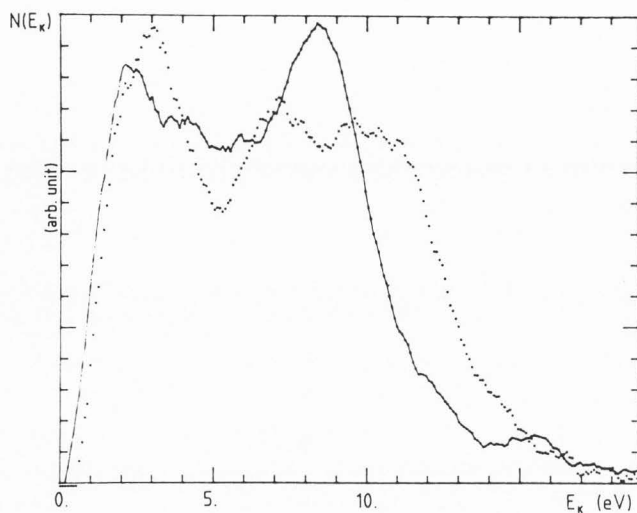


Fig. 5. UPS studies of the Ni-PAN interface: (...) before electrochemical treatment and (—) after treatment.

MODEL OF THE INTERACTION MECHANISM

Molecular model for the interaction between organic molecules and a negatively polarized surface

On the molecular level, the interaction between acrylonitrile and the surface of a negatively polarized electrode can be represented as shown in the schemas of figure 6. In this mode, the spatial representation and electronic populations corresponding to the molecular orbitals of the organic molecules and the emerging metal orbitals appearing at the surface after the oxide reduction process (3d nickel orbitals) are taken into consideration. The acrylonitrile molecule (fig. 6a) is orientated by the electric field of the double layer and strongly polarized. The vinylic π orbital is disturbed, the electronic density decreases on the CH_2 radical which becomes then electrophilic although the electronic density increases on the other extremity of the vinylic bond which becomes nucleophilic (fig. 6b). A strong bonding can establish itself through the overlapping between the 3d metal orbitals and the electrophilic molecular orbitals (fig. 6c). The adsorbed radical ion deactivated by reacting with another acrylonitrile polarized molecule by a mechanism similar to the initial chemisorption (overlapping between the nucleophilic site of the adsorbed molecule and the electrophilic end

of the next molecule). A polymerization reaction (fig. 6d) can, in this way, develop causing modifications to the initial metallic surface, the new solid surface being that of the growing polymer.

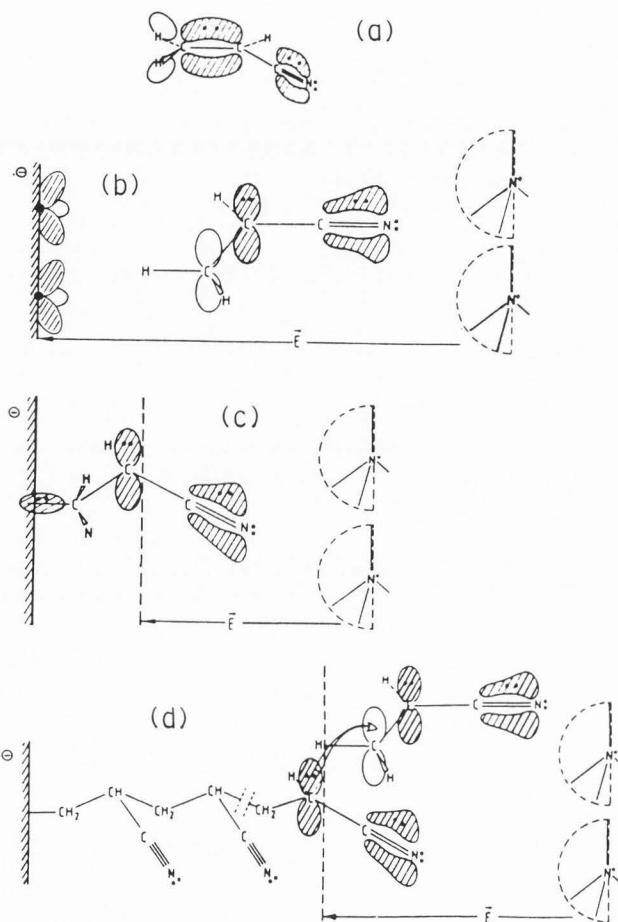


Fig. 6. Molecular model of the AN-surface bond (the dotted line circles represent the structure and the position of the tetraethylammonium ions).

- the acrylonitrile molecule.
- the molecule is oriented and polarized by the double layer field.
- a strong chemisorption bond is established between the nickel surface and the molecule.
- the polymerization process occurs according to the same mechanism.

Energy model for the interaction between organic molecules and a negatively polarized surface

As with all chemical processes the course of grafting and polymerization reactions depends on the energies

of the initial and first states involved. In order to more accurately describe these reactions, it is therefore necessary to take the energy situation of the surface sites representing the initial surface states into consideration (electronic valence levels of the metal, deep electronic levels characteristic of the oxides) as well as those of the molecules (Lowest Unoccupied Molecular Orbital: LUMO, and Highest Occupied Molecular Orbital: HOMO). This energy model is shown in fig. 7. At rest (fig. 7a), the occupied

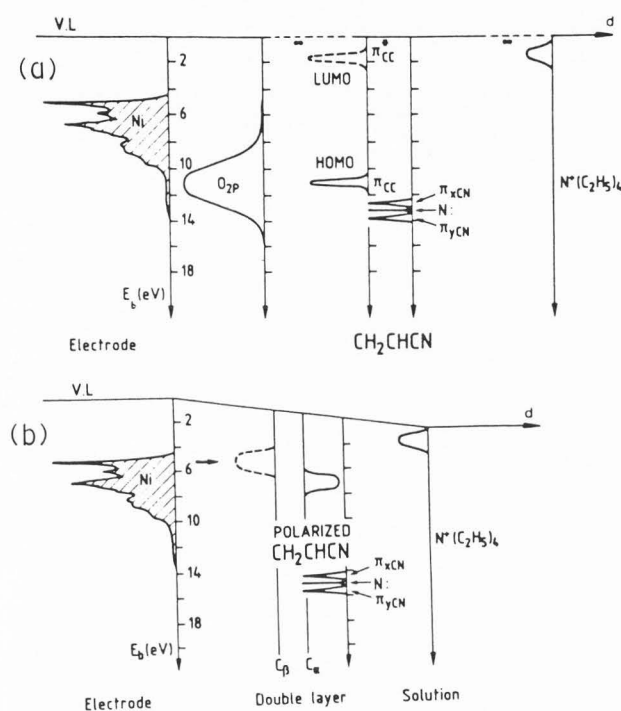


Fig. 7. Energy model of the AN-surface bond (d is the distance from the surface, and E_b is the binding energy of the interacting electronic levels).

a) system out of interaction.
b) polarized system.

electronic levels are located about the 2p oxygen level to the oxidized metallic surface, so their binding energies are too high to give rise to an electron transfer in the LUMO: the setting up of chemical bonds is not possible.

In the presence of the interfacial electric field (fig. 7b) the electronic configuration of the molecule is significantly perturbed: the electron affinity increases (stabilization of the LUMO energy level). Simultaneously, the applied field leads to the reduction of the cathode surface oxide and induces a repopulation of the valence 3d orbitals of the metal. According to the mechanisms involved in the classical chemisorption models, these two phenomena result in a resonance between the nickel d electrons

and the LUMO, which leads to a new chemical bond.

The polymerization reaction has its origin in the decrease of the binding energy of the HOMO, which can then interact with a subsequent molecular LUMO.

CONCLUSIONS

The results presented here emphasize the experimental conditions required for the grafting of a PAN film on a surface of a transition metal.

In particular, the decisive part of an interfacial electric field is underlined: its intensity and direction have a strong influence on the nature of the established bond between the clean metallic substrate and the polymer.

A model of the mechanism involved in the grafting is proposed. It is a solid basis for the building of quantitative models taking into account both the nature and the binding energy of the concerned electronic levels.

Furthermore, experiments are in development for the study of the properties of this interface when submitted to bond operating conditions (temperature, irradiation, electric fields, mechanical stresses).

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DISCUSSION WITH REVIEWERS

G. TOURILLON: I think that the electrochemical curves for both the anodic and cathodic treatments have to be added to support the electrochemical mechanisms: influence of the high electric field near the Ni surface on the polymerization. Authors: This paper has been deliberately devoted to the presentation of results obtained "ex-situ", using several surface spectroscopies: our purpose was to give a detailed description of the nature of the metal-polymer interface. Nevertheless, it is interesting to note that this method allows us to propose a qualitative model for the mechanisms involved in grafting and polymerization of the monomer. But, we agree with G. Tourillon: a complete modelization of these mechanisms implies "in-situ" measurements to be taken into account.

G. TOURILLON: The authors suppose that the same processes occur in the cathodic and anodic domains. I am not sure that this hypothesis is correct because i) the $I = f(V)$ curves are quite different when a Pt electrode is anodically polarized and ii) the anion could be oxidized leading to the formation of radicals which initiate the polymerization of the organic solvent (CH_3CN) and of the monomer (AN).

Authors: We do not suppose that the same processes occur in the cathodic and anodic domains: the comparison must be limited to the main orientation imposed to the monomer by the double layer electric field (fig. 1a and fig. 2a). Indeed, if we are able to give the detailed chemical formula of the polymer obtained in the cathodic domain (fig. 1c), we must limit the description of the polymer obtained in the anodic domain (fig. 2b) to a global formula, R- being as well $\text{H}_3\text{C}-$ as $\text{H}_2\text{C} = \text{CH}-$. Moreover, in the text, we evocate the probable influence of radical initiators on the polymerization mechanisms in the anodic domain.

G. TOURILLON: The reduction of the oxide layer before the grafting of PAN should be reinforced with the ellipsometry results obtained by authors. This step indeed is very important because it means that the surface is "cleaned", during the electrochemical treatment, before the adsorption of the grafting of the organic phase.

Authors: The ellipsometry results obtained "in-situ" are not presented in this paper in consideration of the arguments we developed in response to the first question. In fact, the results

obtained "ex-situ", using Auger spectroscopy coupled with ionic abrasion, and studying very thin films with UPS, are sufficient: they unquestionably show the disappearance of the surface oxide layer simultaneously to the film formation on the metal surface.

G. TOURILLON: In the "Negatively polarized metallic surfaces" section, could you explain "...another activated molecule leads to the polymerization"?

Authors: The interface bonds result on Lewis acid-base reactions, which are also responsible for the polymer film growth. The modified electrode surface is, in fact, constituted of the macro-anionic end of the growing chains, which bear an electronic doublet. This surface is thus a strong Lewis base, and will interact with the Lewis acid end of free acrylonitrile molecules activated and oriented by the double layer electric field. The resulting acid-base reactions (acceptor-donor reaction) govern the polymerization mechanism. This process implies a displacement of the double layer in proportion as the film thickness increases; it implies also a diffusion flow of acrylonitrile molecules from the solution towards the double layer throughout the ionic barrier. These two conditions are satisfied when the faradaic current is large enough to neutralize a significant number of ions. But a large neutralization rate can disturb the double layer homogeneity, and induce the formation of structural defects in the polymer. A compromise must thus be found.

Reviewer IV: I am curious about the geometrical structure of the C-C≡N part of AN; the authors present it as bent in fig. 1c, whereas it is drawn as linear in fig. 6. It is my impression that the authors cannot tell whether it is linear or non-linear from their experiment and that it is probably linear. I wonder how the authors have derived informations (if any on the angle between the C≡N group and the surface (as in fig. 6)).

Authors: In fact, the fig. 6 presented in the copy of this paper for submission

to reviewers had to be corrected: the C-C≡N group is certainly not linear, whereas the -C≡N is oriented towards the film surface. Two sets of results allow us to give this conclusion:

i) heat treatment of the PAN film lead, in a first step, to the cyclization of the chains; a conjugated (-C=N-)_n system appearing in addition to the aliphatic skeleton to form the new polymer (see references 8 and 16). This indicates that the distance between the nitrogen atom of a nitrile group and the carbon atom of the neighbouring nitrile group has a value which has the same order of magnitude than the distance between nitrogen and carbon atoms in the conjugated chain.

ii) Infra-red absorption spectroscopy using a polarized beam shows that the -C≡N groups have a main orientation towards the perpendicular to the substrate surface. The direction of this orientation is given, at the film surface, by MDS. But, it is not yet possible to state precisely the angle values: new experiments must be developed, using, for example, EXAFS techniques.

J. KELBER: The Auger spectra (fig. 4) are not presented on a large enough scale. It is not apparent to me that Ni peaks are present and O peaks absent from spectra c, d and e. It is also possible that Ni signals might be observed for the sputtered films (and not oxygen) because of differences in the mean free paths of the corresponding Auger electrons.

Authors: In an Auger spectrum, the oxygen peak is placed between the low energy nickel peak and the high energy one; this implies that the mean escape depth for oxygen Auger electrons has an intermediate value in respect to those corresponding to the two types of nickel Auger electrons. Moreover, the mean escape depth of the low energy nickel Auger electrons is found in the vicinity of the minimum in the universal curve giving the mean free path of an electron versus its kinetic energy.

Faint, illegible text, possibly bleed-through from the reverse side of the page.