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Department of Applied Chemistry and Chemical Engineering, Claude Bernard University (Lyon I): Current Research in Adhesion Science

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Department of Applied Chemistry and Chemical Engineering, Claude Bernard University (Lyon I): Current Research in Adhesion Science

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This paper reviews the activity in adhesion science of the Department of Applied Chemistry and Chemical Engineering (CNRS, URA 417) of the University of Lyon, France. This work essentially concerns treatments and modifications of surfaces by various chemical, electrochemical and physical techniques—electropolymerization, plasma polymerization, sol-gel processes, phosphatation, etc. Examples of the characterization of these surfaces and that of bonded joints are shown. Emphasis is placed on the possibilities offered by the techniques developed in the laboratory (low-energy electron-induced X-ray spectrometry and the three-point flexure test).

INTRODUCTION

The Department of Applied Chemistry and Chemical Engineering of Claude Bernard University (Lyon I) is a CNRS (National Center for Scientific Research)—associated laboratory with a staff strength of over 50 persons (30 permanent CNRS or university staff and some twenty-odd PhD students) and is essentially concerned with Material Science and Engineering. The central theme of research carried out deals with surface, interface and interphase phenomena. Within this framework, emphasis is placed,

—on the one hand, on the elaboration of film coatings on metallic substrates, i.e.,

- ceramics by sol-gel processes,
 - polymers by electropolymerization and plasma polymerization,
- and ● metals and alloys by electrochemical processes,

—and on the other hand, on surface modifications of metallic or polymer substrates by

- rf and microwave processes,
 - chemical and electrochemical processes,
- and ● ion implantation.

In general, the studies carried out aim at developing multimaterials having properties adapted to specific applications (bonding and painting, anti-corrosion protection and durability, etc.). We shall subsequently review the principal points pertaining to our research in this extremely wide field.

These works, concerning surface treatments and modifications, require highly-performing characterization and analysis tools, and the department possesses the following equipment:

- a surface analysis system comprising X-ray photoelectron (XPS), Auger electron (AES) and Ion scattering (ISS) spectrometers (RIBER SIA 200 with a MAC2 analyzer),
- a low energy electron-induced X-ray spectrometer (LEEIXS) (laboratory-designed system),
- X-ray fluorescence spectrometers (XRFS) (Philips Instruments),
- a scanning electron microscope (SEM) (Philips 515) equipped with an energy-dispersive X-ray spectrometer (EDS) (EDAX 9800), permitting light element detection,
- a glow discharge optical spectrometer (GDOS) (Jobin Yvon),
- A Fourier transform infrared spectrometer (FTIR) (Nicolet 710) equipped with an IRRAS attachment,
- an X-ray diffractometer (XRD),
- impedance meters and set-ups for electrochemical tests and measurements,
- mechanical testing machines (adhesion tests/Young's modulus measurements),
- climatic test cabinets, a salt spray cabinet
- thermal analysis set-ups: TGA, DTA, DSC, dilatometer, conductimeter, etc.

EXAMPLES OF CURRENT RESEARCH

1 Film Coatings

In all cases the metallic substrates are coated in order to elaborate primers capable of ensuring adequate adhesion between these substrates and a large variety of polymer materials (adhesives, paints, varnishes . . .) as well as increased durability of the corresponding systems.

1.1 Films obtained by electropolymerization The discovery of electron-conducting polymers¹ slightly more than ten years ago propelled an intense research activity in the whole of the international scientific community, both with a view to understanding the mechanisms entering into play as well as to improve the synthesis of these products.

Our laboratory became interested in the formation by electropolymerization of polyaniline film coatings on metallic substrates from an aqueous acidic solution of aniline monomer.²⁻⁵ The film formation mechanism implies oxidation of the aniline, with the electrode to be coated acting as the anode. This condition restricts the use

of the metallic materials that can be coated with polyaniline to inert or passivable metals or alloys, e.g. platinum, chromium, stainless steel, Ti6AlV. The conditions of film formation depend on the nature of the metallic substrate to be coated and on the electrochemical conditions used to synthesize the polymer. In the case of 304L stainless steel, the porosity of the film increases with anodic current density, voltage imposed on the electrode and/or the duration of the electrolysis. Best results are obtained for a current density of 0.5 mA cm^{-2} in the galvanostatic mode for an initial voltage of 0.8 V/SCE followed by maintaining at 0.7 V, in the potentiostatic mode. In the case of the titanium alloy Ti6AlV, the combination of a voltage sweep from -0.5 to $+2.0$ V, followed by maintaining at the latter value, allows obtaining a homogeneous coating, that covers the whole of the substrate. Once coated with polyaniline, the metallic substrates are removed from the cell, washed with distilled water, dried, either under dynamic vacuum at room temperature or at atmospheric pressure at temperatures between 50 and 160°C .

Adhesion measurements of the electrodeposited polymer films on these substrates, carried out using the three-point flexure test (cf Chap. 4.2) reveal excellent performances for freshly-prepared films. Maintaining them in a hot and humid atmosphere (70°C , 95% HR) leads to progressive degradation of the polyaniline film/metallic substrate adherence. When water reaches the polymer film/metallic substrate interface, the advantages gained by coating disappear. However, the gain in bonded joint lifetime and the possibility of functionalising the monomer in order to attribute particular properties to the polymer coating, especially the aptitude of forming a greater number of, and/or stronger, chemical bonds with the adhesive, encourages us to pursue our work in this direction, i.e., elaboration of polymer coatings capable of playing a role of adherence promotion between a substrate (whether pre-treated or not) and an adhesive.

1.2 Films obtained by plasma polymerization This process permits the deposition of thin and protective films from a vapour phase at a reduced pressure. Some studies have already shown the possibility of using such polymer films as primers.⁶⁻⁷ The rf system used in this study is of the diode type with plane and parallel electrodes and operates in the RIE mode. The gas used for hydrocarbon deposits is 99.99% pure methane with flow varying from 0 to 50 sccm. The chamber pressure is adjusted within the 0 to 200 mtorr range and generator power is between 0 and 300 W. Thickness and properties of the deposited films are studied as a function of elaboration parameters.⁸ For example, Figure 1 shows the variation of the CK α band intensity obtained in LEEIXS (cf Chap. 4.1) from the polymer films as a function of the generator power, other parameters (pressure and flow of methane) being maintained constant. In the thickness range investigated, the CK α intensity is directly proportional to film thickness. In addition, Figure 2 shows the corresponding variation of a parameter characteristic of adhesion properties and given by the three-point flexure test (cf Chap. 4.2). In most cases the rupture is adhesive between the substrate and the film. Only samples produced at very low power (10 W) present an adhesive rupture at the film/adhesive interface. In the same way, the correct pre-treatment of metallic substrates must be found before plasma polymerization.

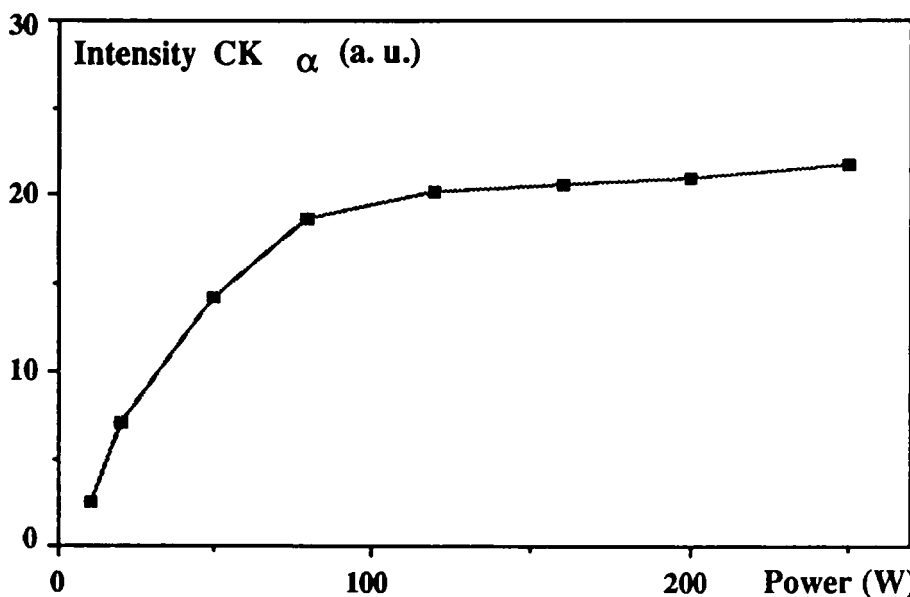


FIGURE 1 Changes in thickness (via CK α intensity measurements) as a function of rf generator power.

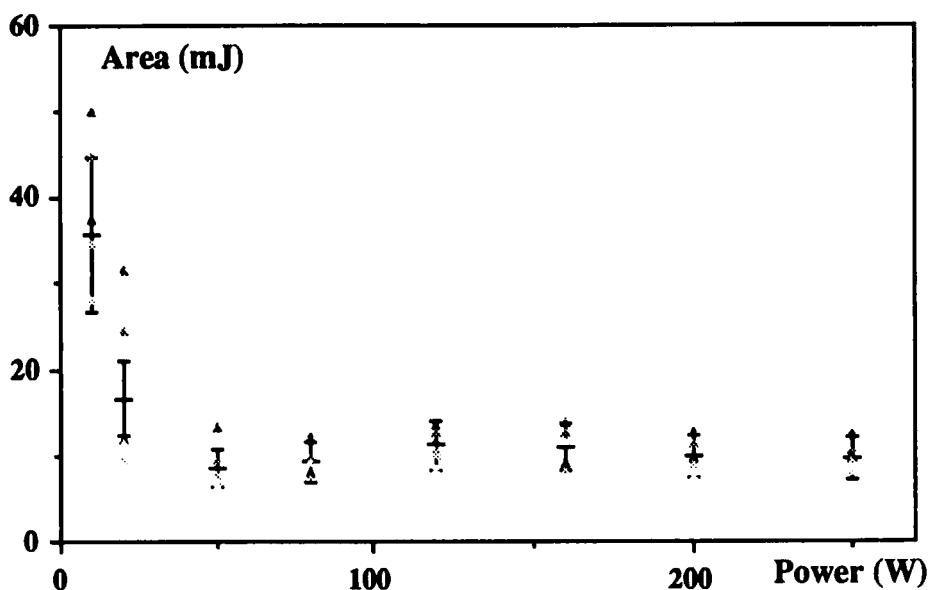


FIGURE 2 Changes in adhesion properties as a function of rf generator power.

1.3 Films obtained by sol-gel processes Coating of metallic substrates by sol-gel processes is an interesting field of research which offers numerous advantages in corrosion protection and electrical and thermal insulation.⁹ Taking into account these properties, we are exploring the possibility of using inorganic thin film coatings obtained in this manner to serve as supports to which polymer materials can sub-

sequently be adhered. With this in view, we are using ormosils, which are polymers having silicate skeletons with organic groups directly linked to silicon by Si—C bonds. These organic groups can either be unreactive or can participate in network formation. Depending on the function, specific properties can be obtained; e.g. with phenyl or methyl groups, hydrophobic products may be produced; on the contrary, using epoxy or amino groups, hydrophilic groups may be prepared. ZrO₂ and pure or modified SiO₂ coatings are currently being deposited on stainless steel and iron sheets by the alkoxide route.

The characteristics (structure, thickness, chemical composition) and anti-corrosion and adhesion properties of the coatings thus prepared are determined by the use of various techniques (XPS, LEEIXS, SEM, pitting potential measurement, adhesion measurements, etc).

2 Surface Modifications

Among the treatments used to modify the surfaces of materials, we shall cite here, essentially phosphatation treatments of galvanized and electrogalvanized steel sheets for automotive industry applications. So-formed conversion layers must possess a number of characteristics which permit formability, weldability, bonding and painting of the sheets as well as good corrosion resistance and long service life. With this aim, the studies carried out in the laboratory¹⁰⁻¹³ deal with (i) the influence of cleaning and refining before phosphatation, (ii) optimization of the phosphatation bath composition (bi- (Zn—Mn; Zn—Ni) or tri- (Zn—Ni—Mn; Zn—Ni—Fe) cation), and (iii) the influence of passive rinsing and drying after phosphatation. The characteristics (crystallographic structure, morphology, roughness, thickness, chemical composition, etc) and anti-corrosion (alkaline resistance) and adhesion properties of the conversion layers prepared in this way are determined by the use of various techniques (XRD, SEM, XRFS, XPS, LEEIXS, GDOS, FTIR, adhesion measurements, etc).

3 Chemical Interactions at Metal/Organic Molecule Interfaces

The chemical characterization of the metal/polymer interfacial zone and of interactions at the interface with the metal require the use and development of specific analytical techniques.

Organic layers on metals have already been studied by various vibrational spectroscopies, including inelastic tunneling (IETS), high resolution electron energy loss (HREELS), surface enhanced Raman scattering (SERS) and Fourier transform infrared (FTIR) methods. Thus, FTIR has been shown to be very useful for characterizing relatively thick layers. In addition, grazing incidence or perpendicularly polarized (to the sample surface) infrared radiation has allowed the detection of a single monolayer or less of an organic material deposited on a good reflecting surface, e.g., a metal.¹⁴⁻¹⁵ In order to investigate chemical reactions between organic materials and metal surfaces, the use of ultra-thin (<10 nm) polymer layers appears to be a good approach. As even the simplest polymers are too complicated to be studied directly, the use of model molecules which are generally monofunctional

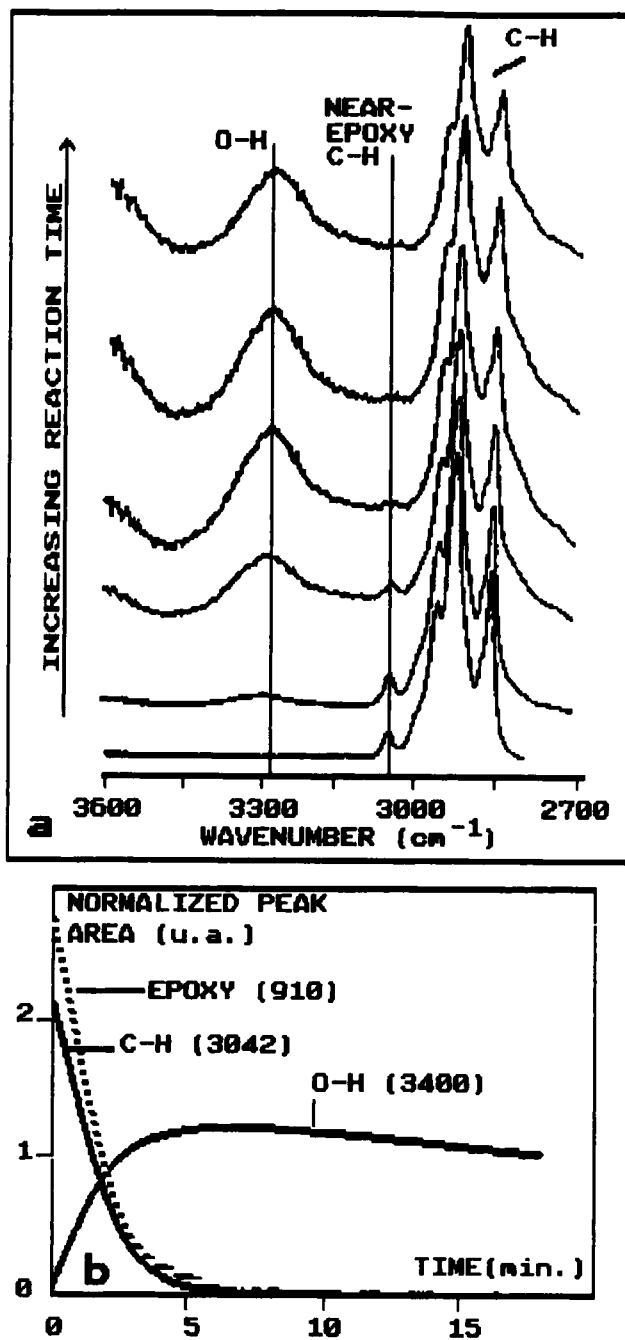


FIGURE 3 FT-IRRAS study of the reaction of diethylenetriamine with epoxyhexane deposited as ultra-thin layer at the surface of a steel (a). Markers used for polymerization kinetics study (b).

and representative for an active group of the polymer considered, constitutes a judicious alternative.¹⁶ Within this same context, the Lewis acidity or basicity of the surface can be determined by studying the interaction between this surface and selected molecular probes whose acidity and basicity are known.¹⁷⁻¹⁸

The example presented here is related to the study of the polymerization of an epoxy resin at a steel surface. As a first step, the reaction of ultrathin layers of model organic materials is performed at the metallic surface and monitored by FT-IR. The model molecules chosen are 1,2 epoxy hexane (standing for the end of the epoxy resin chain) and diethylenetriamine (standing for the hardener). A stoichiometric mixture of these compounds was spread on the polished surface and then spin-coated in order to obtain an ultra-thin layer. Figure 3 shows the spectral changes associated to the chemical reaction leading to the formation of an amino-alcohol. Some accurate markers such as epoxy functions which disappear and hydroxyl functions which appear, can be used for kinetic studies.¹⁹⁻²⁰ The use of such a technique can provide some useful information when the organic material layer is thin enough to obtain spectral data from the metal-organic material surface. In this case, one can expect to detect some reaction between the probe molecules (or a reaction intermediate between these probe molecules) and surface oxides or hydroxides. Complementary results can be obtained at high temperatures and under various atmospheres using a multi-mode heating cell.²¹

4 Specific Characterization Techniques

4.1 Low-energy electron-induced X-ray spectroscopy (LEEIXS) The LEEIXS technique^{22,23} was developed in the laboratory for research purposes, initially in particular to characterize thin oxide films^{12,24,25} (in composition and thickness) grown on metallic substrates (aluminum and its alloys, titanium and its alloys, stainless steel, etc) by various chemical, electrochemical and physical processes.

The instrument is a wavelength-dispersive X-ray spectrometer in which the excitation tube is an electronically-stabilized gas discharge source. Such a system operates as an electron source under the primary vacuum of the spectrometer. Typical operating conditions are in the range 0.5–5 kV with a current between 0.1 and 0.5 mA, the diameter of the electron beam at the sample surface being less than 1 cm². Soft and ultra-soft X-rays emitted in such conditions are dispersed by suitable flat analyzing crystals and detected by a flow-proportional counter. The depth probed depends among others on the incident electron beam energy and the sample nature and typically ranges from 5 to 100 nm. This technique allows both atomic (qualitative and quantitative) and molecular (qualitative) analysis. It is also well suited to light element detection (B, C, N, O, F) and taking into account the source used, to the analysis of insulating samples,²⁶ with the exception of certain polymers which easily degrade under the electron beam.

Concerning polymers, one application of LEEIXS has already been given in Chap. 1.3. Figure 4 describes another example; it shows CK α , OK α and FK α spectra from a polytetrafluoroethylene (PTFE) sample before and after its surface has been subjected to a sodium-naphthalenide treatment for various times, the latter

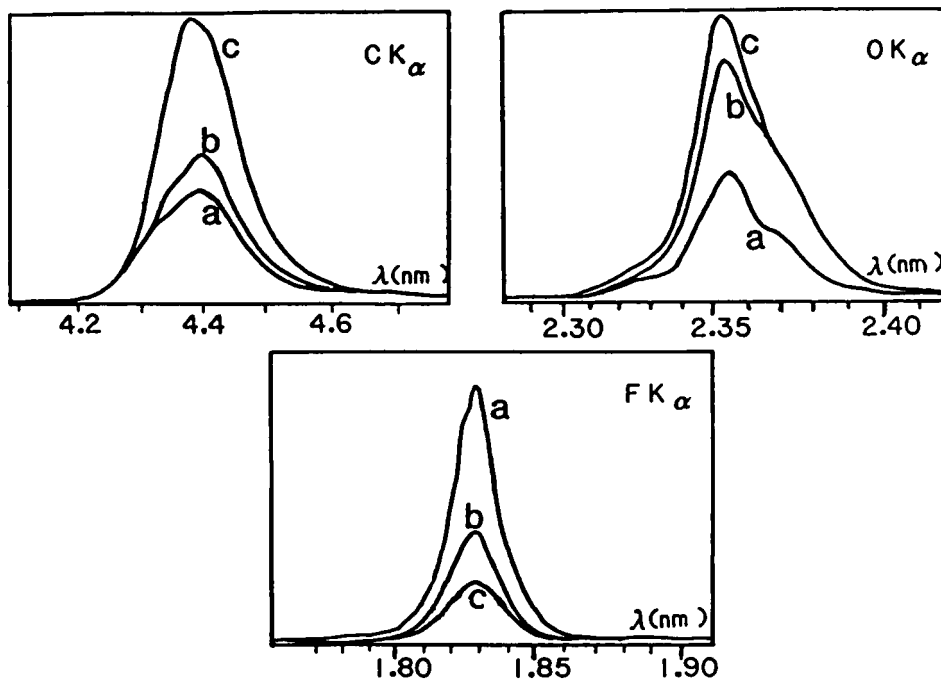


FIGURE 4 $CK\alpha$, $OK\alpha$ and $FK\alpha$ emission bands from a PTFE sample (a) "as received," (b) & (c) after a Na-naphtalene treatment for 30 s and 2 min respectively.

being designed to enhance adhesion properties of these materials which have low-energy surfaces. The spectra shown here illustrate the fact that the reductive treatment is responsible for a defluorination of the polymer surface which then consists mainly of carbon and oxygen. The presence of oxygen results from the fact that the treatment is carried out in ambient atmosphere and that oxidised species are produced when the reactive surface is exposed to air.²⁷

4.2 Three-point flexure test This test is a mechanical method that was initially developed to determine practical adhesion (i.e. the forces or the work required for the disbondment at the interface or within the interfacial region) of adhesive or paint/metallic substrate systems,²⁸⁻³⁰ and is schematically described in Figure 5. This test, which has been normalized,^{31,32} has shown its potential, not only in evaluating the effects of various adherend treatments, but in optimizing, for a given treatment, the experimental conditions to be chosen in order to produce better adhesion. Flat adherend sheets, about 1 mm in thickness, are prepared by die-cutting to provide identically-sized strips (50×10 mm) and are then submitted prior to bonding, to different surface treatments. The single adherend/adhesive specimen geometry has previously been described.³⁰ A computer-controlled three-point flexure tester is used to monitor the cross-head displacement, to record the load/displacement curve and to calculate the parameters of interest {slope of the load/displacement (P vs. d) curve in the linear zone, ultimate load (P_{max}) and displacement (d_{max}) at the moment of sample failure, as well as the corrected area under the load/displacement

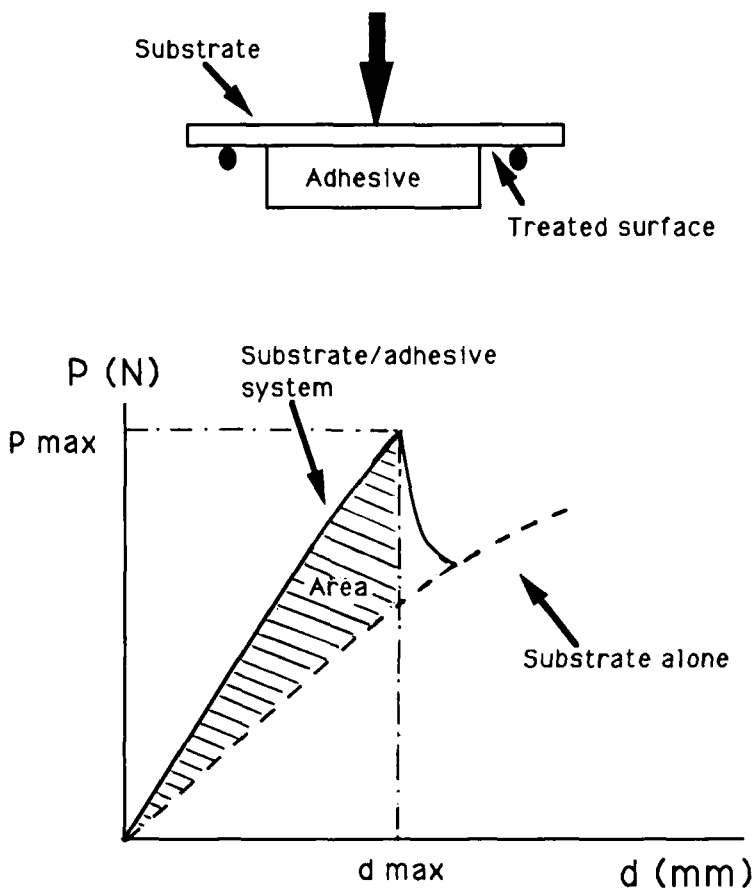


FIGURE 5 Schematic representation of the three-point flexure test and of a typical load (P) vs. displacement (d) curve.

curve}. In addition, this test is used to determine the adhesion of paints on plastics. In this case, the samples should be of the same dimensions but slightly thicker (2–3 mm), in order to possess sufficient rigidity to undergo the test.

The three-point flexure testing machine has also been mounted onto the preparation chamber of the multi-technique surface analysis system (XPS, AES, ISS) available in the laboratory (Figure 6). The samples can thus be delaminated under UHV and transferred directly to the analysis chamber. A secondary electron detector in the system permits selection of the area to be analysed.

CONCLUSION

Adhesion science is pluridisciplinary and requires extended knowledge in several fields. If the emphasis in our laboratory up until now has been on the development of surface treatments and on surface characterization techniques, it is also necessary to deepen our understanding of the fundamental processes and reactions involved

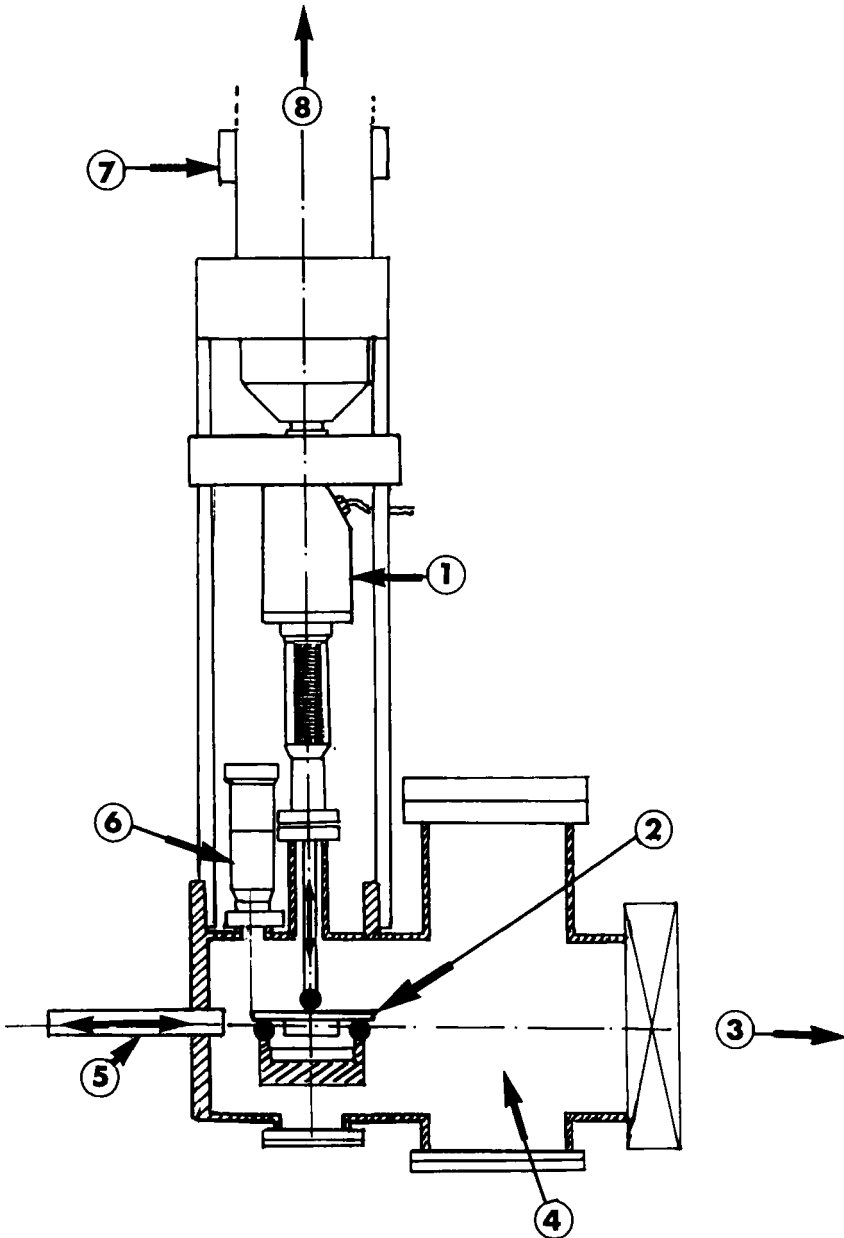


FIGURE 6 Diagram of the three-point flexure testing machine mounted on the preparation chamber of a surface analysis system.

- 1 Load cell;
- 2 Sample in position for three-point flexure test;
- 3 Towards XPS, AES, ISS spectrometer;
- 4 Preparation chamber;
- 5 Sample transfer system;
- 6 Manual system to remove adhesive from substrate after the mechanical test;
- 7 Manual rotation control for sample prepositioning;
- 8 Towards stepping motor, speed reducer and movement translator.

in the interfacial regions of polymer/metal, polymer/oxide, polymer/polymer, . . . systems, both at the time of bonding and after ageing.³³⁻³⁶ More particularly, it is important on the one hand, to understand the reactions between the surface functions of such substrates and the active functions of organic, inorganic or mixed products which may cover them, and on the other hand, to obtain information on the molecular structure and physical properties of the transition region which occurs between the adherend surface and the bulk of the coverage product (adhesive, paint, varnish, . . .). This region, called the "interphase" by Sharpe,^{37,38} is now known to govern the mechanical resistance and durability of joints. The laboratory is already involved in such studies and will be more and more concerned with these problems in the years to come.

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