

ADHESION ASPECTS OF POLYMERIC COATINGS

Volume 2

Editor:

K.L. Mittal

**Adhesion Aspects of Polymeric Coatings,
Volume 2**



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Preface

This volume documents the proceedings of the Second International Symposium on Adhesion Aspects of Polymeric Coatings held under the auspices of MST Conferences in Newark, New Jersey, May 25–26, 2000. The premier symposium on this topic was held under the aegis of the Electrochemical Society in Minneapolis, Minnesota in 1981, the proceedings of which were properly documented in a hard-bound book [1].

As almost 20 years had passed since the first symposium was held so we decided to organize the second event on this topic. In the interim, there had been a great deal of research activity relative to the adhesion aspects of polymeric coatings, so this symposium was both timely (rather overdue) and needed.

Polymeric coatings are used for a variety of purposes, e.g., decorative, protective, functional (as dielectrics or insulators) and a special application of polymeric coatings is their use as lithographic materials for making integrated circuit elements. Irrespective of the intended purpose of the coating, it must adequately adhere to the underlying substrate, otherwise delamination and other undesirable phenomena can occur. So the need to understand the factors which influence adhesion of polymeric coatings and to control it to a desirable level is quite patent. In the last 20 years there have been new theoretical developments and advancements in instrumentation which have helped immensely in the arena of polymeric coatings. The acid-base theory of adhesion has found particular application in controlling the adhesion behavior of coatings.

The technical program for this symposium consisted of 23 papers covering many subtopics dealing with adhesion aspects of polymeric coatings. There were lively and illuminating – not exothermic – discussions, both formally and informally, throughout the symposium. The presenters hailed from many corners of the globe and represented varied disciplines and research interests.

Now coming to this volume (called Volume 2) it contains a total of 13 papers (others are not included for a variety of reasons) addressing many different issues. It must be recorded that all manuscripts were rigorously peer reviewed and suitably revised (some twice or thrice) before inclusion in this volume. So this book is not a mere collection of unreviewed papers – which is commonly the case with many symposia proceedings – rather it represents information which has passed peer scrutiny. Also it should be pointed out that, for a combination of reasons, the publication of this book got delayed but the authors were asked and given the opportunity to update their manuscripts. So the information contained in this book should be current and fresh.

The topics covered in this volume include: factors influencing adhesion of polymeric coatings; ways to improve adhesion; formation and relevance of inter-phase in practical adhesion; adhesion/cohesion in painted plastics; imaging of polymer surfaces; effect of substrate residue (smut) on coating process; surface treatment of metals and glass by silanes; surface modification of polyphenylene sulfide plastics; resin bonding in dentistry; measurement of internal stresses in polymeric coatings; effect of steel surface composition on adhesion of paint; wet adhesion of coatings on wood; and modified tape test to measure adhesion of coatings.

Yours truly sincerely hopes that this book will be of interest to everyone interested or involved in the arena of polymeric coatings. Also it should provide some new ideas as to how to control adhesion durability of coatings in different environments.

Acknowledgements

First, my sincere thanks are extended to my colleague and friend, Dr. Robert H. Lacombe, for taking care of the organizational aspects of this symposium. The comments from the peers are a *sine qua non* to maintain the highest standard of a publication, so I am most appreciative of the time and efforts of the unsung heroes (reviewers) in providing many valuable comments. I am deeply thankful to the authors for their interest, enthusiasm, patience and contribution without which this book would not have seen the light of day. In closing, my thanks go to the staff of VSP (publisher) for giving this book a body form.

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1. K.L. Mittal (Ed.), *Adhesion Aspects of Polymeric Coatings*, Plenum Press, New York (1983).

Interphase: Formation, characterization and relevance to practical adhesion

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Abstract—Epoxy-diamine networks are extensively used as adhesives or paints in many industrial applications. When the precursors are applied onto metallic substrates and cured, an interphase, having chemical, physical and mechanical properties quite different from that of bulk polymer, is created between the substrate and the polymer. Moreover, chemical reactions between diamine and metallic surfaces induce an increase in the practical adhesion (adherence). When the same epoxy-diamine mixtures are applied onto gold coated or polyethylene substrates, the interphase properties are the same as bulk ones. When epoxy-diamine mixtures are applied onto aluminum or titanium alloy surfaces, the glass transition temperature, amine and epoxy reaction extent, the interphase thickness, residual stresses within the interphase, Young's modulus of the interphase all depend on the amine nature (aromatic, aliphatic or cycloaliphatic), the stoichiometric ratio, the processing conditions (time and temperature), the organic layer thickness and the metallic surface treatment. Coating analyses (FTIR, FTNIR, DSC, DMTA, H¹ and C¹³ NMR, SEC, ICP and POM) suggest that diamine monomers chemically react with and dissolve in the metallic hydrated oxide layer. Then, metallic ions diffuse through the organic layer to form a complex by coordination with diamine monomers (chelate or ligand). Metal-diamine complexes are insoluble, at room temperature, both in diamine as well as in DGEBA monomers and they induce a phase separation during the curing cycle of the epoxy-diamine precursors. Furthermore, the chemical bonding of diamine monomers to the metallic surfaces and the diamine-metal crystal orientation parallel to the metallic surface within the interphase lead to chemical, physical and mechanical properties to the epoxy-diamine network which are different from those of the bulk.

Keywords: Epoxy-diamine networks; practical adhesion; interphase; diamine-metal chemical reactions.

1. INTRODUCTION

Epoxy-diamine mixtures are extensively used as adhesives or paints in many industrial applications. When they are applied onto metallic substrates and cured, epoxy-amine liquid monomers react with the metallic oxide and/or hydroxide to form chemical bonds [1, 2] increasing practical adhesion (or adherence) between

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the epoxy polymer and the substrate surface [3, 4]. Different studies concern the influence of the metallic substrate nature on the prepolymer cross-linking. Some authors have shown a catalytic effect of the substrate on the cross-linking mechanisms and the prepolymer adsorption onto metallic surfaces [5]. Others have attempted to determine the existence of monomer/substrate specific reactions. As an example, Dillingham and Boerio [6] have studied the polymerization of a diglycidyl ether of bisphenol A (DGEBA) and a triethylene tetramine (DGEBA-TETA) system applied onto aluminum by using both FTIR and XPS. Close to the polymer/metal interface, the hardener is partially protonated by aluminum hydroxides. Moreover, the polymerization is catalyzed by the presence of hydroxide acid groups leading to an interphase formation. Nigro and Ishida [7] have studied, by using FTIR, an epoxy/BF₃-monoethylamine system applied onto polished steel. The epoxy conversion rate is more important in the polymer/metal interfacial region suggesting the existence of chemical reactions with the steel surface. The epoxy prepolymer was applied onto the steel surface (without hardener), and the same phenomenon was still observed suggesting that the chemical species formed at the steel surface were able to catalyze the homopolymerization of the epoxy monomer. Gaillard and coworkers [8-9] have shown that the DGEBA-DDA polymerization rate was faster on the zinc surface of galvanized or electrogalvanized steel than on polished steel. They concluded that this was due to a catalytic effect of zinc metallic ions leading to a higher extent of cross-linking. Some researchers have studied the adsorption of various monomers, used as adhesives, at the substrate surface [10-12]. Kollek [13] studied, using FTIR, the polymerization of a diglycidyl ether of bisphenol A and a dicyandiamide (DGEBA-DDA) system applied onto aluminum and observed that both the DDA and the DGEBA monomers were adsorbed onto the aluminum oxide surface. For the DDA monomer, the adsorption was due to the acidic proton of the aluminum oxide. For the epoxy monomer, the adsorption was achieved by the oxirane (or epoxy) ring opening. Unfortunately, only a few papers [14-17] have dealt with molecular structures formed within the interphase region.

Moreover, when epoxy resins are applied onto metallic substrates and cured, intrinsic and thermal residual stresses develop within the entire organic layer [18]. Intrinsic stresses are produced as a result of the mismatch between the active sites of the metallic substrate and the organic network and/or the formation of the polymer network. Thermal stresses are mostly developed during cooling [19] and are the result of thermal expansion mismatch between the metallic substrate and the polymer or cure-induced shrinkage of the organic layer [20]. Whatever their source, these residual stresses reduce the practical adhesion and may induce cracks in coating materials [21-23] resulting in a drop of the overall performance of adhesives or paints. To gain a better understanding of epoxy/metal adhesion requires a full knowledge of chemical and physical reactions which take place in the epoxy/metal interphase [24, 25]. Thus, the polymer/substrate interphase is a complex region containing gradients of residual stresses, as well as allowing structural rearrangement, intermolecular and inter-atomic interactions and diffu-

sion phenomenon [24]. When the adhesion of epoxy/metal systems failed, it was possible not only to correlate the residual stresses at the interphase/metal interface to practical adhesion but also to correlate the theoretical adhesion and durability to the presence or not of some chemical species [26]. However, in such systems, chemical and physical mechanisms leading to the interphase formation were not well understood. The aim of this paper was to develop an understanding of this interphase formation and to characterize it using model epoxy-amine systems.

2. EXPERIMENTAL

2.1. Materials

2.1.1. Substrates

The metallic substrates used were commercial 0.516 ± 0.005 mm thick 5754 aluminum alloy from P echiney and 0.600 ± 0.005 mm thick Ti6Al4V titanium alloy from A erospatiale. Titanium and aluminum sheets were made into squares of dimensions 100×100 mm². Before any monomer application, aluminum and titanium substrate surfaces were ultrasonically degreased in acetone for 10 min. and wiped dry. However, some titanium and aluminum panels were also degreased and chemically treated. Titanium samples were immersed in a solution of 10 g/l of ammonium difluoride for 2 min. at room temperature, rinsed in running tap water for 1 min., immersed in deionized water for 5 min. and wiped dry. Aluminum panels were degreased and submerged in a solution of 250 g/l of sulfuric acid, 50 g/l chromium acid and 44 g/l aluminum sulfate at 60 C for 20 min., rinsed and dried as titanium. After surface treatment, all substrates were kept in an air-conditioned room (22 ± 2  C and $55 \pm 5\%$ R.H) for 2 h. Some aluminum sheets were coated with gold (≈ 100 nm) using a SCD005 Sputter Coater from Bal-Tec.

2.1.2. Monomers and polymers

The bifunctional epoxy prepolymer used was a liquid diglycidyl ether of bisphenol A (DGEBA, $M = 348$ g/mole, DER 332) from Dow Chemical. The cycloaliphatic diamine curing agent used was isophorone-diamine (IPDA or 3-aminomethyl-3,5,5-trimethylcyclohexylamine) from Fluka. An aromatic diamine, (4,4'-methylenebis(3-chloro-2,6-diethylaniline) or MCDEA) from Aldrich and an aliphatic diamine, (polyoxypropylene diamine or D400) from Texaco were also used. Epoxy prepolymer and curing agents were used without further purification. Assuming a functionality of 4 for the diamines and 2 for the epoxy monomer, a stoichiometric ratio ($a/e = \text{aminohydrogen/epoxy}$) equal to 1 was used throughout the work. Homogeneous mixtures of DGEBA and diamine were achieved by stirring under vacuum (≈ 1 Pa) at room temperature for 1 h (Rotavapor RE211 from B uchi, Switzerland) to avoid air bubble formation. The epoxy-amine adhesive cure cycle [27-29] was adapted to obtain both the maximum of the cure conversion, i.e. the highest glass transition temperature denoted T_g^x , and the thickest interphase formation. For IPDA, the curing cycle was: 3 h at 20 C, 20 \rightarrow 60 C

(2°C/min.), 2 h at 60°C, 60 → 140°C (2°C/min.), 1 h at 140°C, 140 → 190°C (2°C/min.), 6 h at 190°C, cooling (8 h) in the oven to 20°C; for MCDEA: 3 h at 20°C, 20 → 60°C (2°C/min.), 2 h at 60°C, 60 → 160°C (2°C/min.), 4 h at 160°C, 160 → 190°C (2°C/min.), 9 h at 190°C, cooling (8 h) in the oven to 20°C; and for D400: 3 h at 20°C, 20 → 60°C (2°C/min.), 2 h at 60°C, 60 → 100°C (2°C/min.), 3 h at 100°C, cooling (8 h) in the oven to 20°C.

2.1.3. Sample preparation

Several layers of an adhesive tape (5413 from 3M), approximately 50 µm thick, were applied all around the periphery of 100 x 100 mm² treated metallic sheets to obtain the desired liquid coating thickness. The epoxy-diamine mixtures were poured onto the metallic surfaces and spread with a cylindrical glass rod. For bulk materials, 10 x 10 x 100 mm³ bars were prepared using a silicone (RTV 501 from Rhône-Poulenc) or PTFE mould. Only the central parts of the bars were used for analysis. After curing and cooling down, the coating thicknesses (from 40 to 1500 µm) were determined using an EG-100 Digital Linear Gauge (from Ono Sokki Co, Japan) having a ± 2 µm sensitivity.

2.1.4. Monomer analysis

To characterize the changes in monomers, both the liquid monomers DGEBA and IPDA were applied between two chemically treated metallic substrates (100 x 50 mm²) to form a 110-150 µm thick liquid film and kept at room temperature for 3 h in a desiccator under continuous nitrogen flow to prevent any monomer carbonization or oxidation. Then, the liquid monomers were scraped from the metallic surfaces (and will be called “modified monomers” in the following) with a PTFE spatula and stored in polyethylene vials under a nitrogen atmosphere.

2.2. Experimental techniques

2.2.1. Differential scanning calorimetry (DSC)

DSC experiments were carried out in a Mettler DSC 30 apparatus to determine the glass transition temperature (T_g) of epoxy resins. Sealed aluminum pans containing 15-20 mg of resin were heated from -50°C to 250°C at a rate of 10°C/min under a continuous flow of U-grade argon. Samples were weighed using a Mettler balance having a ± 1 µg sensitivity. The calorimeter was calibrated with both indium and zinc. The glass transition temperature (onset) was determined with a ± 0.5°C sensitivity. To evaluate the variation in T_g with the coating thickness, the (T_g)_{eq} value at thickness (i) was calculated using:

$$(Tg)_{eq} = \frac{h_i Tg_i - h_{i-1} Tg_{i-1}}{h_i - h_{i-1}} \quad (1)$$

where T_{g_i} corresponds to the T_g of a h_i thick coating and T_{g_{i-1}} value corresponds to the glass transition temperature of a h_{i-1}, thick coating.

2.2.2. Dynamic mechanical thermal analysis (DMTA)

Dynamic viscoelastic measurements on coatings, after removal from the metallic substrate, were performed in a Rheometrics Solids Analyzer RSA II apparatus, using the tensile mode to determine the storage (E'), and loss (E'') moduli as well as the ratio $E''/E' = \tan \delta$ as a function of temperature. Samples ($4 \times 40 \text{ mm}^2$) were heated from -150°C to 250°C using a heating rate of $2^\circ\text{C}/\text{min}$ by a forced convection oven using a nitrogen stream. The sample was deformed sinusoidally to a controlled strain amplitude of 0.05% at a fixed frequency of 1 Hz. Measurements were made at 30 s intervals.

2.2.3. Fourier transform infrared and near-infrared spectroscopy (FTIR, FTNIR)

An infrared spectrometer (FTIR Magna-IR 550 from Nicolet) was used with Omnic FTIR software. An Ever-GloTM source was used along with a KBr beam-splitter and DTGS-KBr or MCT/A detector. The mid-infrared spectra were recorded in the $400\text{--}4000 \text{ cm}^{-1}$ range and in the $4000\text{--}7000 \text{ cm}^{-1}$ range for the near-infrared. A transmission accessory was used for bulk or free standing film characterization. For the bulk material, KBr was mixed in a 100:1 ratio with the various epoxy resins which had been ground cryogenically. This mixture was then pressed under vacuum to obtain disks. For analysis, pure KBr disks were used as background. For each analysis, 64 or 96 scans were collected at 4 cm^{-1} resolution.

The cure conversions for epoxy and amine groups were calculated by using, respectively, the 4530 cm^{-1} epoxy combination band and the 6500 cm^{-1} amine band [30]. The 4623 cm^{-1} aromatic C-H ring stretch combination band was considered as reference. Thus, the amine (X_a) and the epoxy (X_e) conversions were determined using the ratio of the respective peak areas (A) by:

$$X_a = 1 - \frac{(A_{6500}/A_{4623})_i}{(A_{6500}/A_{4623})_{i=0}} \quad \text{and} \quad X_e = 1 - \frac{(A_{4530}/A_{4623})_i}{(A_{4530}/A_{4623})_{i=0}} \quad (2)$$

Once again, to evaluate the X_a and X_e variation versus the coating thickness we calculated the $(X_a)_{eq}$ and $(X_e)_{eq}$ values at thickness (i) using:

$$(X_{a,e})_{eq} = \frac{h_i(X_{a,e})_i - h_{i-1}(X_{a,e})_{i-1}}{h_i - h_{i-1}} \quad (3)$$

According to Bentadjine [31], it is possible to correlate the stoichiometric ratio (a/e) to the X_a/X_e ratio as shown in Fig. 1. Then, the variation of the equivalent stoichiometric ratio $(a/e)_{eq}$ versus the coating thickness can be determined.

2.2.4. Nuclear magnetic resonance (NMR) spectroscopy

For proton and carbon Nuclear Magnetic Resonance (^1H and ^{13}C NMR) a Bruker AC 400 spectrometer was used with the sodium salt of deuterated trimethyl silyl propionic acid (TSPd₄) as the internal standard. Analyses were carried out at 293 K using deuterated water in which pure IPDA and modified IPDA were com-

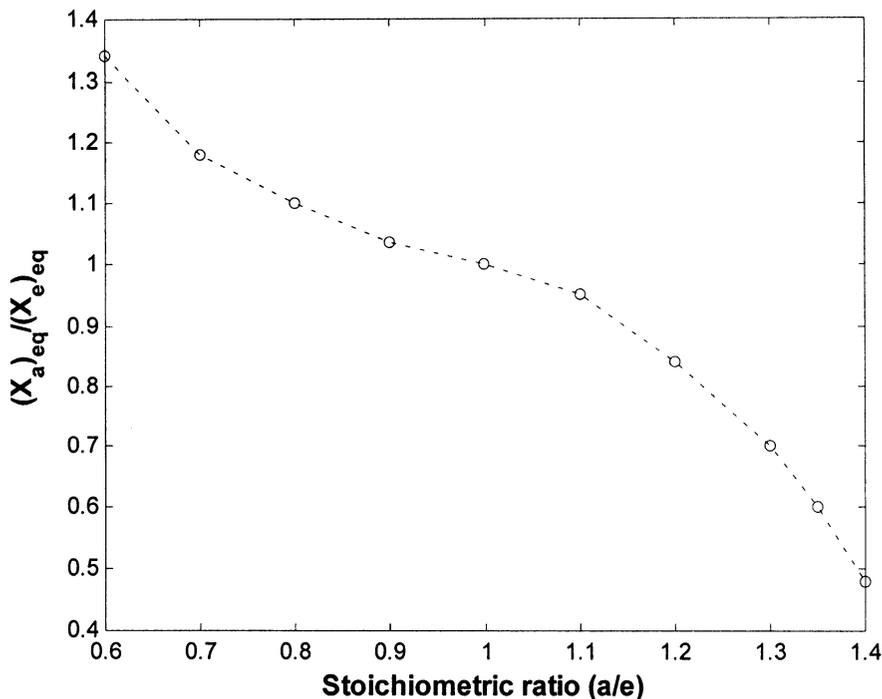


Figure 1. Variation of the $(X_a)_{eq}/(X_e)_{eq}$ ratio as a function of the stoichiometric ratio (a/e).

pletely soluble. By comparing pure IPDA and modified IPDA spectra it was possible to determine the differences in chemical shifts for the equivalent carbon nuclei.

2.2.5. Inductively coupled plasma (ICP) spectroscopy

An ICP spectrometer (Modula by Spectro Analytical Instruments) was used with a 2.5 kW plasma generator at 27 MHz. It was fitted with various detectors (an UV (0.75 m, 2400 grooves mm^{-1} ; 160–480 nm) monochromator, UV (0.75 m, 3600 grooves mm^{-1}) polychromator, and visible (0.75 m, 1200 grooves mm^{-1}) polychromator). A cross-flow nebulizer was used to introduce the liquid sample. Distilled water was used for dilution.

2.2.6. Size exclusion chromatography (SEC)

A Waters apparatus was used with double detection (UV Waters 484 Tunable Absorbance Detector at $\lambda = 254$ nm and Waters 410 differential Refractometer) and a Waters 510 HPLC pump. The elution solvent used was tetrahydrofuran (THF) and the separation was carried out on two styrene-divinyl benzene columns (Nucleogel 100-5 and 500-5 from Macherey-Nagel) with a flow rate of 1 ml/min. The average molar mass calibration curve was constructed from monodispersed polystyrene standards and used to correlate the retention time to the mass average molar mass (\bar{M}).

2.2.7. Polarized optical microscopy (POM), scanning electron microscopy (SEM) and electron microprobe analysis (EMPA)

Drops of diamine or epoxy-diamine mixture were confined between two glass plates and mounted on a hot plate under the optical microscope (Laborlux 12POLLS from Leica equipped with a hot plate FP82 from Mettler and a CCD-IRIS color video camera from Sony). Samples were heated from 30°C to 190°C at 10°C/min. A scanning electron microscope (Philips XL20) fitted with an electron microprobe analysis accessory (Edax-Econ4) was also used. Samples were neither coated with gold nor with carbon. The accelerating electron voltage was 5 kV, the electron spot diameter for microanalyses was about 200 nm and the tilt angle used was 15°.

2.2.8. Free corrosion potential and pH measurements

Different aqueous solutions with isophorone diamine (IPDA) were prepared. The pH's of the solutions were measured at room temperature (22°C) using a PHN 850 pH-meter from Tacussel equipped with a combined electrode (Pt-Ag/AgCl). The pH variation versus the diamine concentration in aqueous solution is shown in Fig. 2. The basic behavior of IPDA is clearly shown. For DGEBA/IPDA prepolymer with a/e = 1, the IPDA concentration is equal to 20 wt% which corresponds to a pH value of 12. The same basic behavior was obtained for aqueous D400 (pH = 12.1) and MCDEA (pH = 10.3) monomer solutions. Free corrosion potential (or open circuit potential) measurements were carried out by using a Tacussel Potentiostat (PRT 40-1X) with a combined Pt electrode (Ag/AgCl).

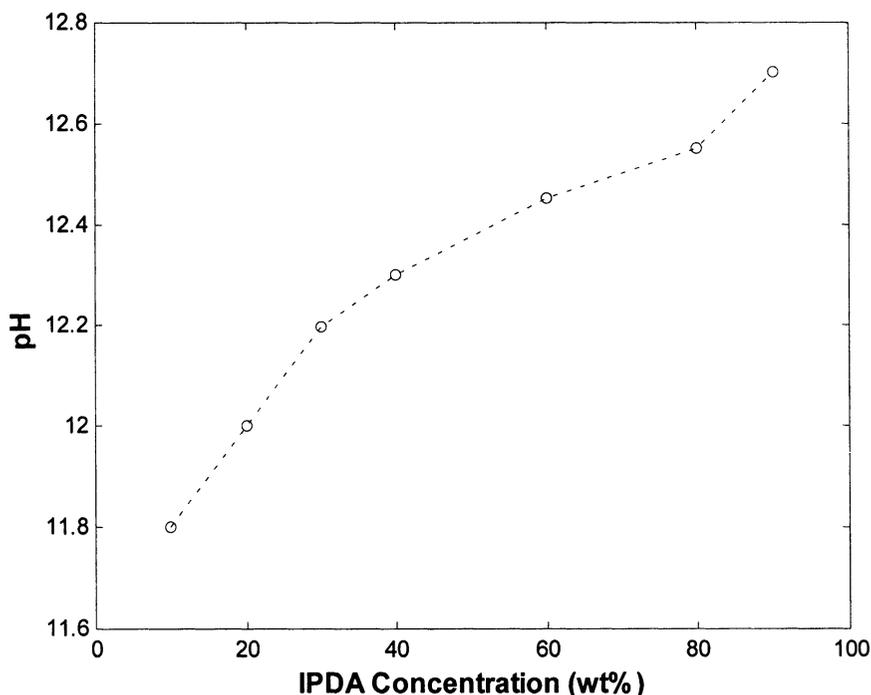


Figure 2. pH variation of aqueous solution as a function of IPDA concentration.

3. RESULTS AND DISCUSSION

3.1. Bulk and coating characteristics

According to the curing cycle mentioned above, the maximum glass transition temperatures (T_g^∞) of DGEBA/IPDA, DGEBA/MCDEA and DGEBA/D400 bulk epoxies were 163°C, 188°C and 34°C respectively. For these bulk materials, the amine conversion (X_a) and the epoxy conversion (X_e) were equal to 1. These values are in good agreement with the previous works [27-29]. Variations in the glass transition temperatures $(T_g)_{eq}$ versus DGEBA/IPD coating thickness applied onto both degreased titanium and aluminum are shown in Fig. 3. Variations in the equivalent stoichiometric ratio $((a/e)_{eq})$ versus the thickness of DGEBA/IPDA coatings applied onto degreased titanium and aluminum substrates are shown in Fig. 4. Regardless of coating thickness, for the coatings applied onto a gold coated substrate, the $(T_g)_{eq}$'s were equal to the (T_g^∞) of the cured bulk DGEBA/IPDA material and the equivalent stoichiometric ratio $((a/e)_{eq})$ was equal to 1. Similarly, for coatings applied either onto degreased titanium or aluminum that were thicker than 400 μm or 200 μm respectively, $(T_g)_{eq}$ and $(a/e)_{eq}$ were all equal to those of the cured bulk DGEBA/IPDA system. For the thinnest coatings ($\leq 50 \mu\text{m}$) applied onto titanium or aluminum, $(T_g)_{eq}$ values were quite different ($\approx 129^\circ\text{C}$ and 108°C respectively) from the bulk ones (163°C) and the equivalent stoichiometric ratios $(a/e)_{eq}$ were 1.19 and 1.14, respectively. Thus it can be assumed that for these thin coatings, a different epoxy network was formed. For coating thicknesses between $50 \leq h \leq 400 \mu\text{m}$ for Ti and $200 \mu\text{m}$ for Al, a gradient region was observed. In all the following work, the interphase thickness (or width) will be defined as the region where the properties are different from those of the bulk. In the case of the DGEBA/IPDA coatings, the interphase is thicker for the titanium substrate (400 μm) than for the aluminum one (200 μm). So, we can assume that the dissolution rate of TiO_2 amorphous oxide is higher than that of the Al_2O_3 amorphous oxide. According to Ellingham [32], the standard free energies at room temperature of formation of Al_2O_3 and TiO_2 crystalline oxides are equal to 250 and 210 kcal/mol O_2 , respectively. In a first approximation, we can assume that the amorphous oxide layer formed on aluminum alloy was more stable than the one obtained on titanium alloy. Thus, for the same diamine monomer, the dissolution rate of TiO_2 should be higher than that of Al_2O_3 leading to a wider interphase for TiO_2 , and this is observed experimentally. The large interphase thickness also means that for a 1 mm thick coating on degreased titanium, the first 400 μm from the substrate surface corresponds to the interphase and that only the remaining 600 μm will have the same properties as the DGEBA/IPDA bulk epoxy. Also, we observe that the interphase thickness depends on the substrate nature (Fig. 4) as well as on the basic behavior of the amine as shown in Fig. 5. The formation of such a thick interphase has to be explained.

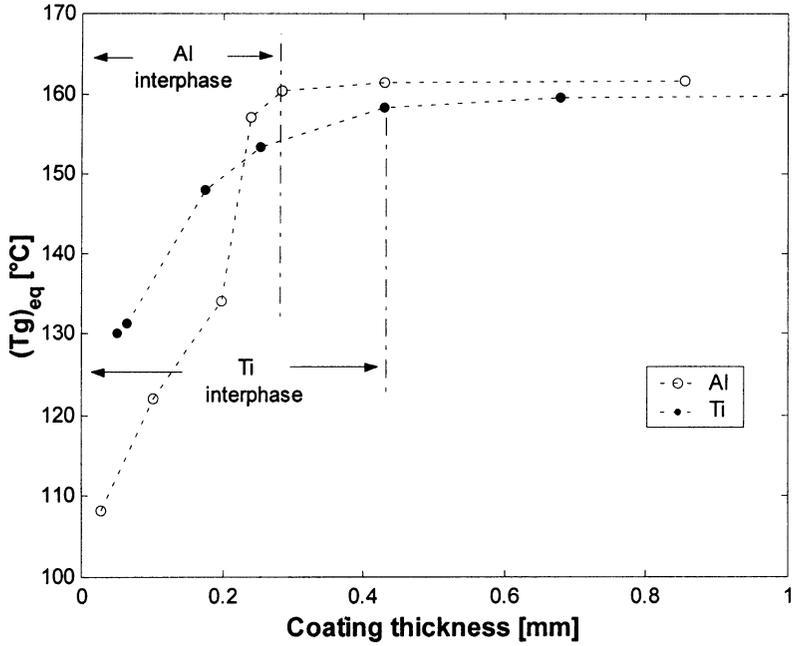


Figure 3. Variation of the equivalent glass transition temperature versus the coating thickness for degreased titanium and aluminum substrates.

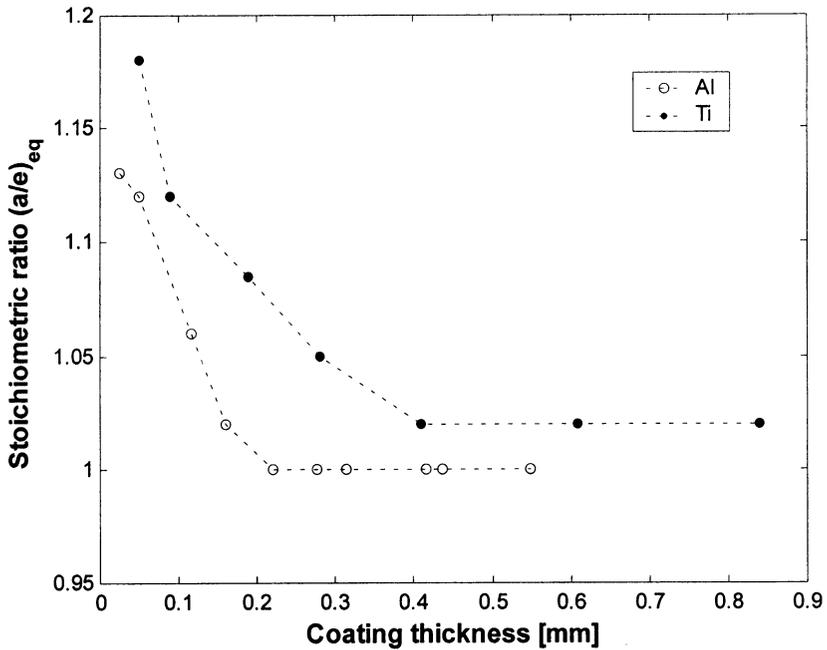


Figure 4. Variation of the equivalent stoichiometric ratio $(a/e)_{eq}$ as a function of the coating thickness for both degreased titanium and aluminum substrates.

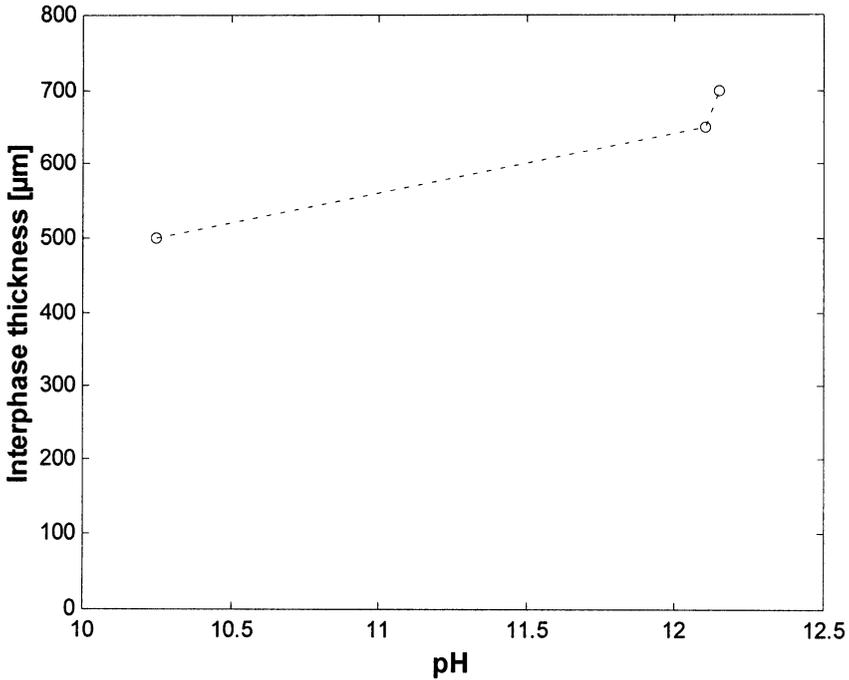


Figure 5. Variation of the interphase thickness versus the pH of monomer aqueous solution.

3.2. Monomers characterization

To characterize the chemical changes occurring, DGEBA and IPDA liquid monomers were placed between two chemically treated metallic substrates (Ti or Al) and kept at room temperature for 3 h. Then, Ti or Al modified monomers were scraped from their metallic substrates with a PTFE spatula and visually compared to the pure monomers. Both pure monomers (DGEBA and IPDA) were transparent. No color change of the DGEBA monomers after application onto titanium or aluminum was observed. The IPDA monomers from both aluminum and titanium became milky white (Fig. 6). After two hours within test tubes, a separation was observed. The floating part remained transparent while the precipitate was milky white. One drop each of the precipitate from both Ti and Al modified IPDA were placed between two glass plates and observed using a polarized optical microscope (Fig. 7). Crystals in the modified IPDA liquid were observed corresponding to a new chemical product formed when the IPDA monomer reacted with the metallic oxide and/or hydroxide surface of both titanium and aluminum.

Taking into account the basic nature of the pure diamine curing agent, a dissolution of the metallic oxide or hydroxide by the amine is assumed when the monomer is applied onto the metallic substrate. The free potential variation versus the immersion time for chemically etched titanium immersed in a 20 wt% aque-

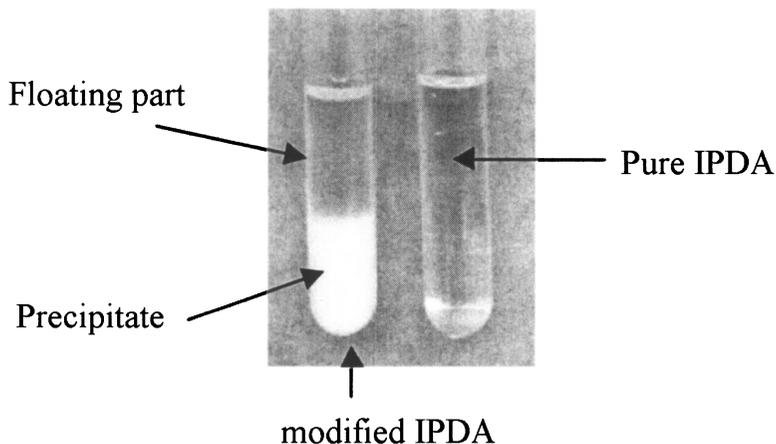


Figure 6. Photographs of pure IPDA and IPDA modified either on titanium or aluminum.

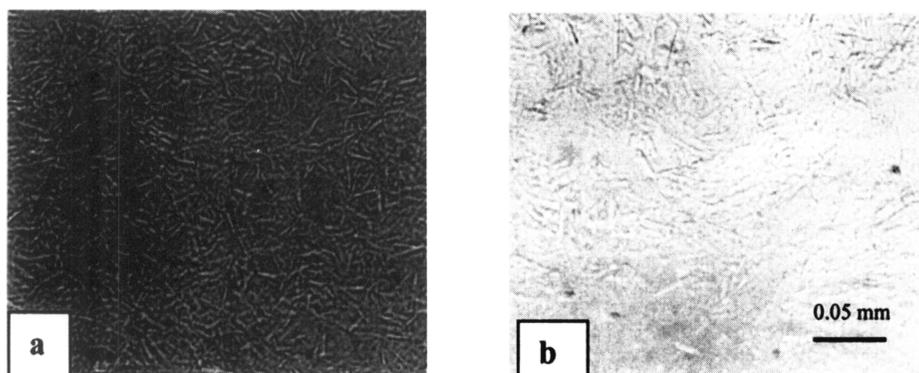


Figure 7. POM micrographs of the modified IPDA precipitates obtained after application onto titanium (a) and aluminum (b) substrates.

ous IPDA solution is reported in Fig. 8 and it suggests a dissolution of the metallic oxide surface. A comparison of the SEM micrographs (Fig. 9) of the degreased titanium and aluminum surfaces to the ones obtained after an application of IPDA for 3 h and rinsing with acetone shows indisputably a chemical attack of the metallic surfaces by the liquid IPDA monomer. The dissolution of metallic oxide or hydroxide surface layers may induce a metallic ion diffusion within the IPDA liquid monomer. Experimentally, this was observed by ICP analysis of pure IPDA and the precipitate portion of Ti and Al modified IPDA as reported in Fig. 10. The presence of titanium or aluminum is shown clearly in the modified IPDA monomer spectrum. Thus the hypothesis of the dissolution of the titanium or aluminum oxide and/or hydroxide by the basic diamine monomer is strengthened. FTIR spectra of pure IPDA and modified IPDA after application onto aluminum,

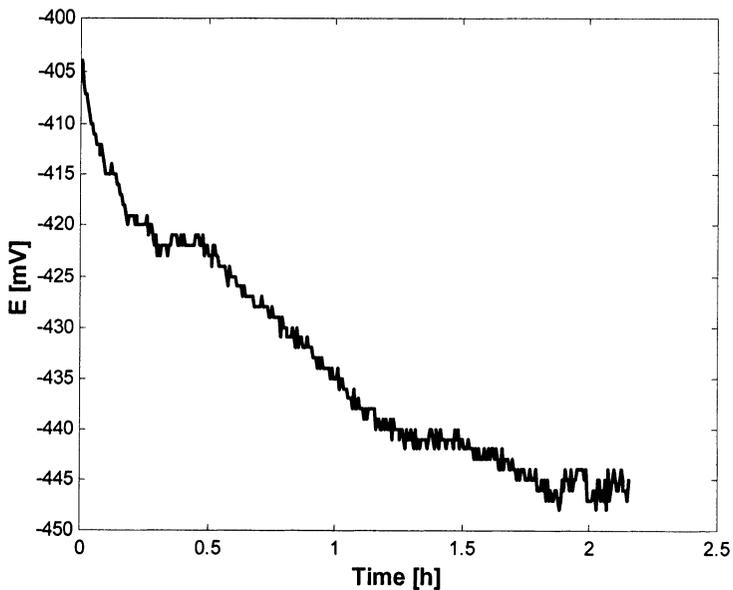
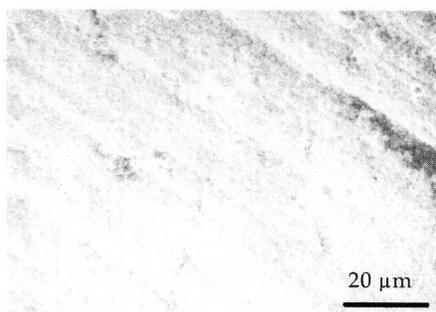
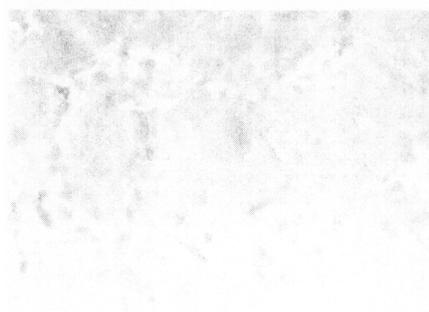


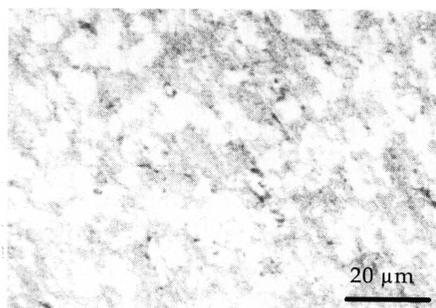
Figure 8. Variation of the free potential versus time for a chemically etched titanium substrate immersed in an aqueous solution of IPDA (20 wt%).



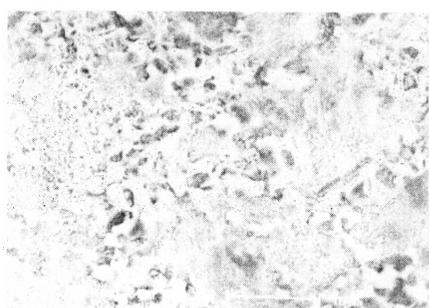
Initial aluminum surface



Initial titanium surface



Aluminum surface after IPDA removal



Titanium surface after IPDA removal

Figure 9. SEM photomicrographs of the initial surfaces of degreased titanium and aluminum substrates and after application for 3 h of liquid IPDA monomer and removal using acetone rinse.

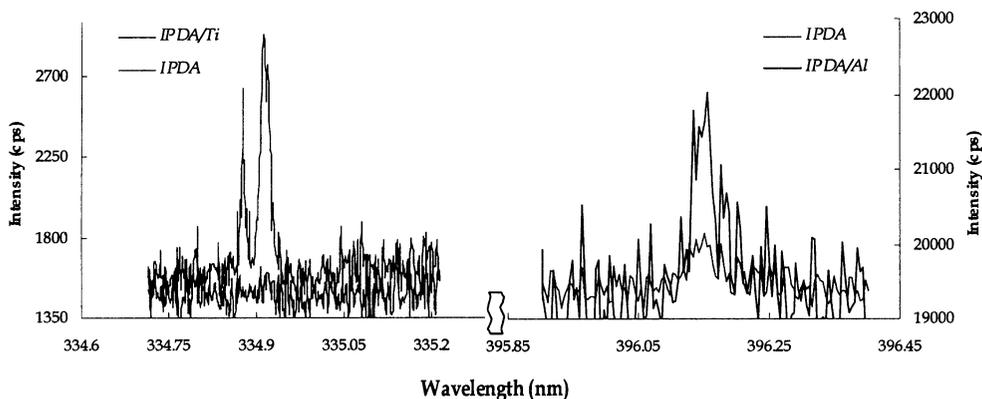


Figure 10. ICP spectra of pure IPDA and titanium and aluminum modified IPDA.

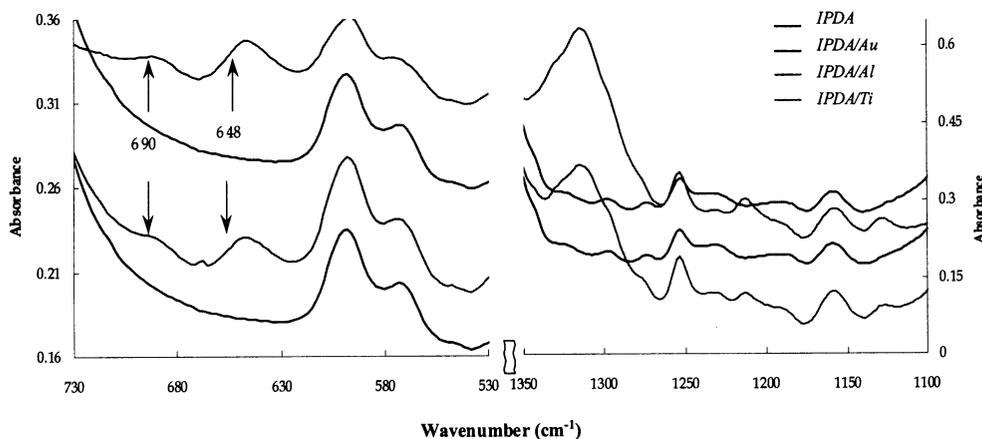


Figure 11. FTIR spectra of pure IPDA and IPDA modified on titanium, aluminum or gold coated substrates.

titanium or gold coated substrate are shown in Fig. 11. The spectra of pure IPDA and modified IPDA after application onto a gold coated substrate or the floating portion of the modified IPDA on aluminum and titanium are identical. However, new bands (between $1100\text{--}1350\text{ cm}^{-1}$ and $600\text{--}700\text{ cm}^{-1}$) are observed only when IPDA was applied onto titanium and aluminum substrates. FTIR results confirmed that no chemical reaction occurred when coatings were applied onto the gold coated substrates. The diamine monomer (IPDA) clearly reacts with both titanium and aluminum substrates. Fig. 12 shows the reflectance index (RI) SEC spectra obtained from pure diamine monomer (MCDEA) and modified MCDEA with both titanium and aluminum substrates. New small peaks are observed which correspond to $\bar{M}_w = 1014\text{ g/mol}$ for titanium and $\bar{M}_w = 1011\text{ g/mol}$ for aluminum. These values are twice higher than the pure MCDEA monomer mass average molar mass ($\bar{M}_w = 489\text{ g/mol}$).

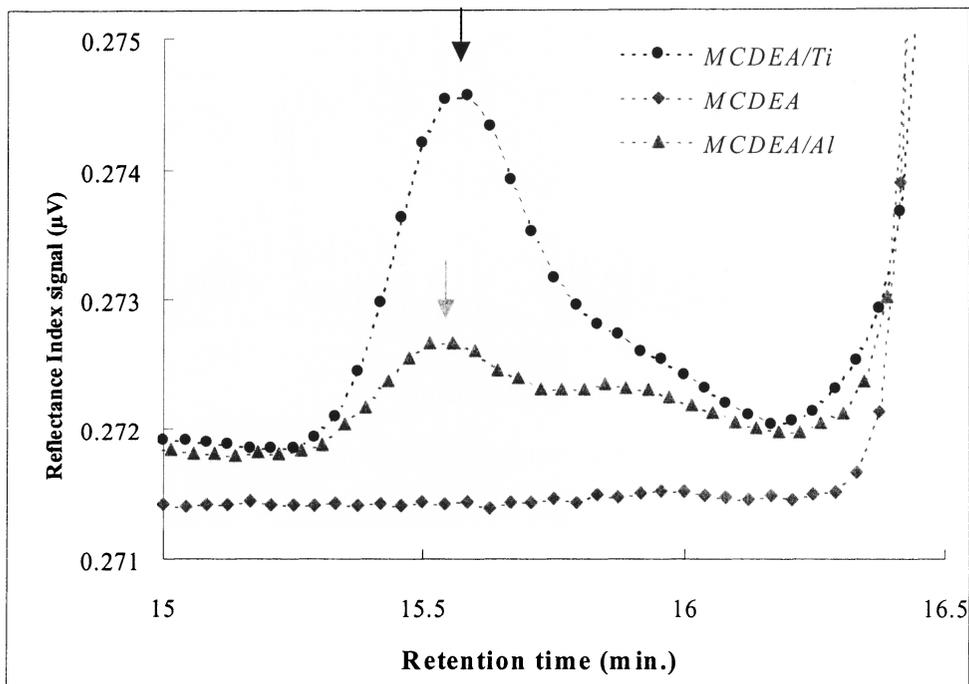


Figure 12. SEC spectra of pure MCDEA and MCDEA modified on titanium and aluminum substrates.

To characterize the chemical bindings that may appear between the IPDA monomer and metallic ions, nuclear magnetic resonance (NMR) spectroscopy was used. Pure IPDA monomer was actually a mixture of 25% “cis” and 75% “trans” isomers and the corresponding conformations and the carbon atom labeling are shown in Fig. 13. Peak assignment of pure IPDA was achieved using ^1H , ^{13}C and 2D NMR spectra as reported elsewhere [33, 34]. Spectra of pure IPDA monomer and modified IPDA applied onto titanium and aluminum were also obtained. After a complete peak assignment, it can be noted that some of the characteristic nuclear resonance frequencies vary (magnetic shielding) when IPDA was applied onto titanium and aluminum. From the differences between characteristic resonance frequencies, chemical shifts can be calculated [35]. Fig. 13 shows also the NMR chemical shifts for various carbon atoms when IPDA was applied onto titanium and aluminum. Only carbon atoms associated with nitrogen atoms or neighboring carbon atoms were affected when the monomer was applied onto metallic substrates and the shift was found to be the same regardless of the isomer. The chemical shifts obtained for aluminum were about two to three times higher than the ones observed on titanium. From these results, it can be assumed that the bond between amine groups and metallic ions results from the electron-rich nitrogen atom donating its lone pair to the electron-deficient metallic center. Thus, organo-metallic complexes were created by coordination bindings. When the com-