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Is gold always chemically passive?

Study and comparison of the epoxy-amine/metals interphases

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Abstract

When epoxy-amine liquid mixtures are applied onto metallic substrates (such as Al, Ti, Sn, Zn, Fe, Cr, Cu, Ag, Ni, and Au), concomitant amine chemisorption and metallic surface dissolution occur, leading to organo-metallic complex formation. The interphase formation was studied, using two different amines as hardener (IsoPhoroneDiAmine and DiEthyleneTriAmine). If the complex concentration within the liquid amine or epoxy-amine prepolymer was higher than its solubility limit, the complexes will crystallize. Sharp needle-like crystals were only observed with metal-IPDA organo-metallic complexes. A lot of metals are widely used as reactive substrates with gold as a reference, which is considered chemically inert. It is misleading, since it will be shown in this article that gold reacts with amine, just as the other metals.

Keywords: Chemisorption; Diffusion and migration; Surface chemical reaction; Gold; Solid-liquid interfaces; Epoxy; Amine; Metal-polymer interphase

1. Introduction

On one hand, gold is well known to be chemically inert [1,2], and often used as a reference substrate since it supposedly never reacts with any coating. On the other hand, some chemists hardly study gold reactions, especially the gold self-assembled monolayer (SAM), and the gold-organic molecule junction using scanning tunnelling microscopy [3–6]. In addition, gold is now well known as a catalyst [7,8], even without any stable oxide (its absence is unique to gold). As epoxy-amine liquid prepolymers are extensively applied onto metallic substrates and cured to obtain painted materials or adhesively bonded structures, they were studied as coating on different metallic substrates (such as Al, Ti, Sn, Zn, Fe, Cr, Cu, Ag, Ni, Au), with a particular emphasis put on gold. The overall performance of such systems depends on the substrate properties, the coating properties, and the interphase created between the polymer

layer and the substrate. When epoxy-amine liquid mixtures are applied onto metallic substrates, amine chemisorption concomitant with metallic surface dissolution occur, leading to the organo-metallic complex formation [9–11]. When a metal oxide is exposed to a very basic environment (such as amine coating), the oxides and hydroxides disassociate exposing the underlying metallic ions (which are Lewis acids) [12] and then the amine groups (which are Lewis bases) can easily react with the metallic surface, leading to the metal-amine complexation [13,14].

Furthermore, when the solubility product is over and that the complex geometry makes their crystallization possible, the organo-metallic complexes may crystallize. These crystals induce changes of mechanical properties (effective Young's modulus, residual stresses, practical adhesion, durability [15–23] ...). The interphase formation depends on many parameters, such as hardener nature, curing cycle, viscosity of the prepolymer mixture [15,17–19].

In this work, two different amines were used and mixed to the DGEBA (DiGlycidyl Ether of Bisphenol A) epoxy monomer (a/e = aminohydrogen function/epoxy function = stoichiometric ratio = 1) to form bulk materials or coatings. The IPDA (IsoPhoroneDiAmine) is a cycloaliphatic diamine which may crystallize after modification (i.e., after being applied onto

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the metal surface leading to a chemical reaction between the liquid amine and the metal), whereas the DETA (DiEthylene-TriAmine) is an aliphatic triamine. The modified DETA never crystallizes, even after 3 h in contact with aluminium. The parameters determining the interphase formation were evaluated, and correlated to the change of mechanical properties observed by many authors [9,10,15–19,21,24–26].

2. Experimental

2.1. Materials

All the metallic substrates used were very pure: min. 99.87% Ag, 99.5% Al, 99.99% Au, 99.99% Cr, 99.9% Cu, 99.5% Fe, 99.0% Ni, 98.8% Sn, 99.6% Ti, and 99.95% Zn. The aluminium was a commercial 1050 alloy from P  chiney, France, and the other metals were from Goodfellow. Before any prepolymer application, all the metal substrates were ultrasonically cleaned in acetone for 10 min and dried by dabbing with absorbent paper. Then, only aluminium substrates were submerged in a sulfo-chromic solution (250 g L⁻¹ of sulfuric acid ($d = 1.84$), 50 g L⁻¹ of chromium VI oxide and 87.5 g L⁻¹ of aluminium sulfate octadecahydrate) for 1 h at 60 °C and then rinsed in running water for 1 min. Finally, the aluminium substrates were dipped in deionized water for 5 min and dried by dabbing with absorbent paper. After such surface treatment, all the metallic substrates (except gold) were covered by their oxide and hydroxide. These hydroxide layers were quite stable over a pH range depending on the metal [27].

After the surface treatment, all substrates were stored for 2 h in a room with controlled temperature and humidity (20 ± 2 °C and $50 \pm 5\%$ r.h.) before polymer application. The humidity and temperature control lead to the formation of a reproducible oxide and hydroxide layer for each used metal. As many experiments were carried out, the metal oxide formation had to be reproducible. Of course, the layer formed on different metals can have very different properties. The DiGlycidyl Ether of Bisphenol A (M.W. = 348 g mol⁻¹, DGEBA DER 332 from Dow Chemical, see Fig. 1) was used as epoxy prepolymer and the curing agents were either IsoPhoroneDiAmine (IPDA, see Fig. 2) from Fluka or DiEthyleneTriAmine (DETA, see Fig. 2) from Aldrich. Assuming a functionality of 4 for IPDA, 5 for DETA and 2 for the epoxy monomer, the stoichiometric ratio (a/e, aminohydrogen/epoxy) was equal to 1. The pure IPDA monomer supplied by Fluka was a mixture of 25% *trans* and 75% *cis* stereoisomers.

To control the extent of chemical reactions between the metallic surface and the liquid monomers, which leads to the formation of the interphase, the liquid epoxy-amine mixtures were kept in contact with the metallic surface at room temperature for 3 h before starting the desired adhesive curing

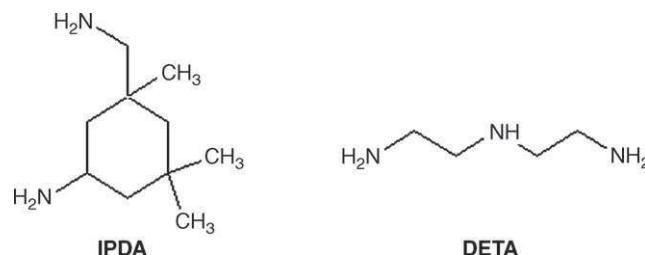


Fig. 2. Chemical structure of the amines (IPDA and DETA).

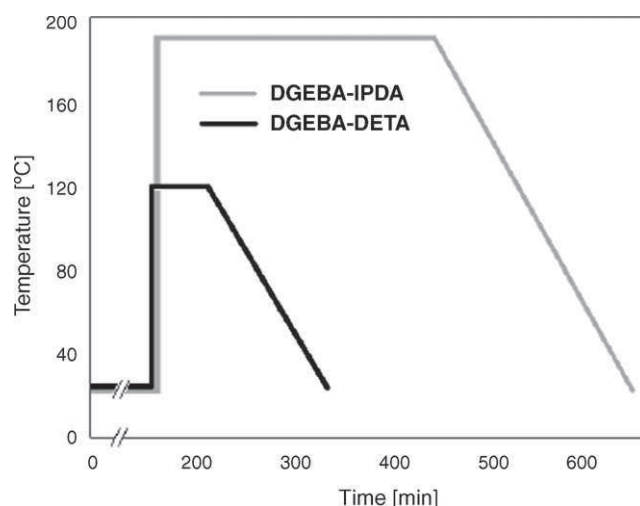


Fig. 3. Curing cycles used for both DGEBA–DETA and DGEBA–IPDA systems.

cycle (e.g., see Fig. 3). Indeed, a very important parameter controlling the interphase formation is the liquid/solid contact time at room temperature before the curing cycle. The polymerization (i.e., reaction between the amine and the epoxy monomers) and interphase formation (i.e., reaction between amine and metal) are in competition. Then, the chosen curing cycles allowed the maximum conversion (i.e., the maximum glass transition temperature, $T_g = 159$ °C for the DGEBA–IPDA system and $T_g = 132$ °C for the DGEBA–DETA system, outside the interphase), according to previous works on epoxy resins [28–30], and the maximum interphase formation [15]. Finally, the amines can be placed between two metal sheets for 3 h in order to study the organo-metallic complexes formation. The amines reacting with the metals will be called “modified amine”: the modified amines are a mixture of pure amine and organo-metallic complexes.

2.2. Inductively coupled plasma spectroscopy (ICP)

Inductively coupled plasma (ICP) is an analytical technique used for the detection of trace metals in environmental samples. The primary goal of ICP is to get elements to emit characteristic

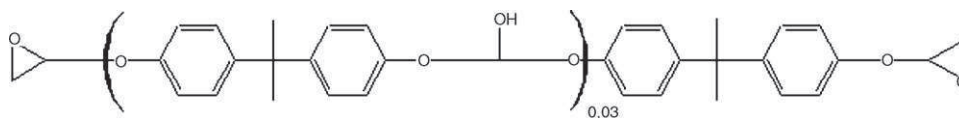


Fig. 1. Chemical structure of the epoxy monomer DGEBA, der 332.

wavelength specific light which can then be measured. An ICP spectrometer (simultaneous VISTA from VARIAN) was used with a 40 MHz generator and a CCD detector (70908 pixels, wavelength from 167 to 785 nm) to determine the metal ion concentration within the liquid amine after 3 h of liquid/solid contact. Distilled water was used as the diluting agent (each sample – 1–10 mg – was diluted in 50 mL of distilled water).

2.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) experiments are able to measure the amount of heat absorbed during the glass transition by observing the difference in heat flow between the sample and a reference. The DSC experiments were carried out in a Mettler (DSC 30) apparatus to determine the glass transition temperature (T_g) of the epoxy networks. Aluminium pans containing 15–20 mg of resin were heated from $-50\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under a continuous flow of argon. The reference is an empty aluminium pan. The glass transition temperature (onset) was determined with a $\pm 1\text{ }^{\circ}\text{C}$ sensitivity.

2.4. Polarized optical microscopy (POM)

The optical microscope used was a Laborlux 12POLS from Leica equipped with a CCD-IRIS color video camera from Sony.

2.5. Nuclear magnetic resonance (NMR)

Nuclear magnetic resonance (NMR) spectroscopy is one of the principal techniques used to obtain physical, chemical, electronic and structural information about molecules. It is a powerful technique that can provide detailed information on the topology, dynamics and three-dimensional structure of molecules in a solution and in the solid state. It is a very selective technique, distinguishing among many atoms within a molecule or collection of molecules, the same type of atoms that differ only in terms of their local chemical environment: in

this work, the amine molecules can contain metallic ions and complex with them, but the amine molecules can also be unmodified. Indeed, in order to see the complexation between the DETA and metals, ^{13}C NMR was carried out on pure and modified DETA. The studied amines were diluted at 10 wt.% in mass in deuterated water. Before any dilution could occur, N_2 gas was injected in deuterated water in order to prevent any reaction between the amine and the atmospheric CO_2 . Nuclear magnetic resonance was carried out using a Bruker DRX 400, operating at 100.62 MHz and at room temperature, in the NMR centre of the “Fédération des Polyméristes Lyonnais” (USR-59/CNRS). The used reference was the TSPd_4 or sodium salt of deuterated trimethyl silyl propionic acid.

3. Results and discussion

When liquid epoxy-amine prepolymers were applied and cured on metallic substrates, interphases were created within the organic layer at the vicinity of the metal surface.

3.1. Interphase formation mechanisms

In previous works [9–11], it was shown that the interphase formation was the result of the dissolution of the metallic surface layers, concomitant with the ion diffusion through the liquid prepolymer: when the oxide is exposed to a very basic environment (such as amine coating), the oxides and hydroxides disassociate exposing the underlying metallic ions (which are Lewis acids) [12]. Then the amine groups (which are Lewis bases) can easily react with the metallic surface.

In order to detect the dissolution phenomenon, pure amine (either DETA or IPDA) was applied onto metallic sheets. After 3 h, the metallic surfaces were scraped with a PTFE spatula. This method is misleading since some amine remains on the substrate, but after ICP analyses, it nevertheless gives a minimum amount of dissolved ions. The method, consisting in scraping the metal surface with a spatula, could also lead to mechanical removal of un-reacted metal and over-estimation of the quantity of dissolved ions, but the spatula is very soft (fully made of Teflon) and then this phenomenon is limited. For the sake of simplicity, this method was used as a qualitative method (and not quantitative one): it can be assumed that the real number of metallic ions dissolved by the amine is higher than the counted ions. The “modified” IPDA or DETA (i.e., the amine reacting with the metal) were then analyzed by ICP (see Fig. 4), and the modified DETA by ^{13}C NMR (see Fig. 5). Metallic ions were detected in the modified amines irrespective of the amine and the metal substrate used (excepted IPDA applied on the gold substrate), and the DETA seemed to dissolve a little bit more metal than the IPDA amine. Gold was not detected in the gold-modified IPDA, probably because of the detection limit of the apparatus. As the gold sample was the smallest substrate, the mass of the gold-modified IPDA was about $1\text{ }\mu\text{g}$, which led to difficulties in the ICP analyses. In addition, the ^{13}C NMR realised on pure and modified DETA showed that all the modified DETA peaks were shifted compared to the pure DETA peaks, irrespective of the metal

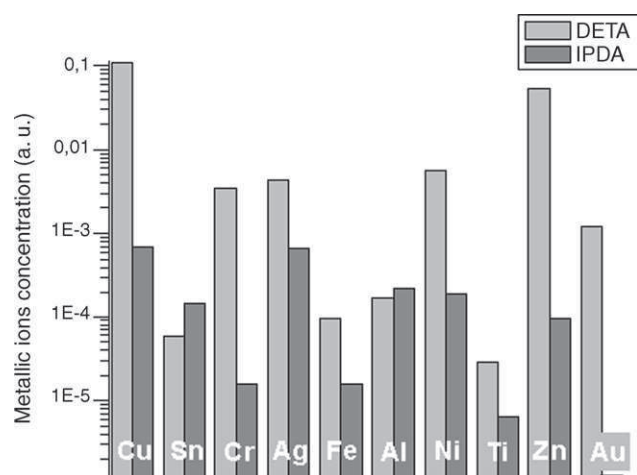


Fig. 4. Metallic ion concentration in the modified amine vs. metal used as a substrate.

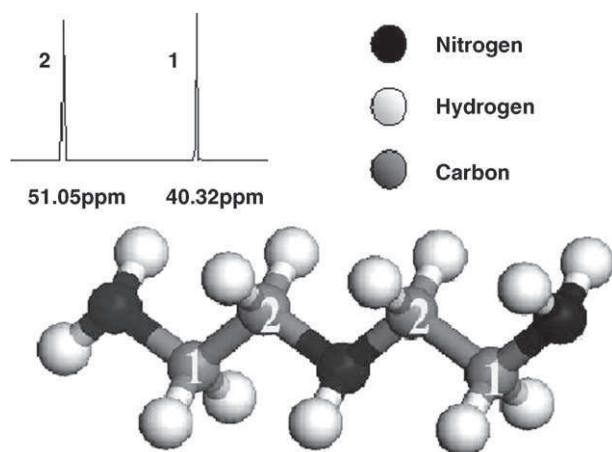


Fig. 5. ^{13}C NMR spectrum of pure DETA linked with the DETA molecule.

used. In particular, for gold, peaks were detected at 40.17 ppm and 50.73 ppm for the peaks 1 and 2, respectively (see Fig. 5): the difference with the pure DETA was for gold a shift of 0.22 ppm for the peak 1 and 0.42 ppm for the peak 2.

The amine chemisorption on oxidized and/or hydrated metal surfaces concomitant with the partial dissolution of the surface oxide metal substrate was observed according to the base characteristics of the amine monomer. Then it could be assumed that either:

- metal ions diffuse within the liquid monomer mixture and react with the amino groups of the hardener to form organo-metal complexes or,
- organo-metallic complexes form on the metal surface layer and diffuse within the liquid monomer mixture (epoxy-amine).

After application onto the metallic surfaces, both amines were modified to form an organo-metallic complex, and the initial liquid epoxy-amine mixture was transformed into a

mixture of organo-metallic complexes and pure (i.e., unmodified) amine with pure epoxy prepolymer.

3.2. Crystallization of “modified” IPDA

If the complex concentration within the liquid amine or epoxy-amine prepolymer is higher than its solubility limit and the complex geometry makes their crystallization possible, the organo-metallic complexes may crystallize. Sharp needle-like crystals were previously observed [9,10,15,16,19] with Al and Ti modified IPDA, whereas modified DETA never crystallized (even after 3 h in contact with any metal). Fig. 6 represents pictures from modified IPDA (i.e., IPDA applied on different metals for 3 h). Irrespective of the metal used, sharp needle crystals could be observed in modified IPDA, showing that IPDA reacted with all the metals (including gold). The IPDA could also react with atmospheric carbon dioxide to form carbonates, but it was possible to distinguish organo-metallic crystals from IPDA carbonates, as the organo-metallic crystals looked like sharp needles and were single crystals (extinction was observed using POM) whereas the carbonates were fluffy and simply in a solid state (extinction was not observed using POM) [16].

In order to characterize the crystallized organo-metallic complexes, and considering their initial dimensions, it was necessary to increase their size. Therefore, only the Al-IPDA complexes were recrystallized: the recrystallization needed a minimum quantity of complexes. This quantity was obtained only with aluminium and presented in a previous article [16]. Then, Al-IPDA crystals were analyzed by X-ray diffraction: Al-IPDA crystallized in a monoclinic system and the space group was Pc. The unit cell was described as an IPDA molecule, added to a water molecule and a carbon dioxide molecule. The IPDA was the *trans* isomer, as expected, because the IPDA mixture was 75% of *trans* isomer and 25% *cis* isomer, and the geometry of *trans* was more suitable for crystallization. Only the *trans* isomer crystallized after modification by aluminium (no *cis* isomer was observed by X-ray diffraction), even if both

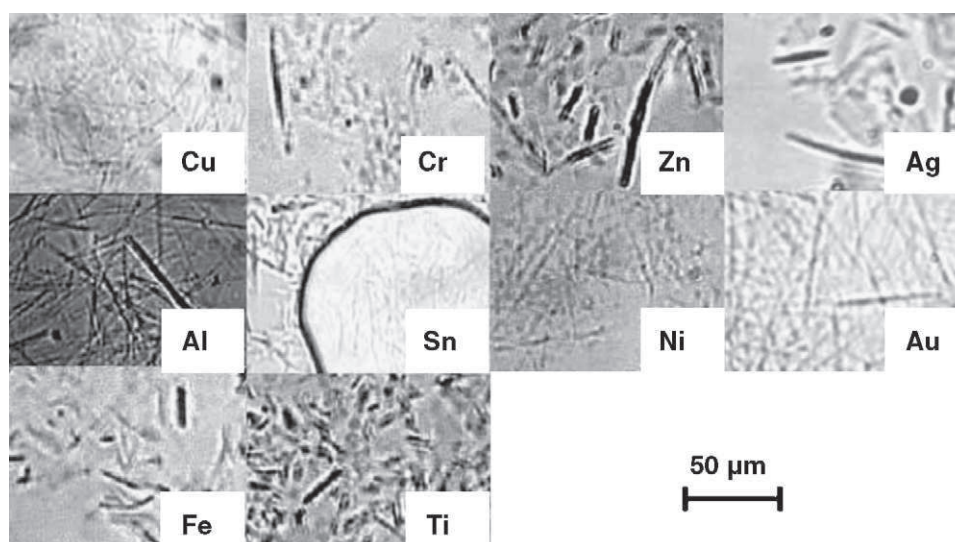


Fig. 6. POM pictures of metal-IPDA organo-metallic crystals.

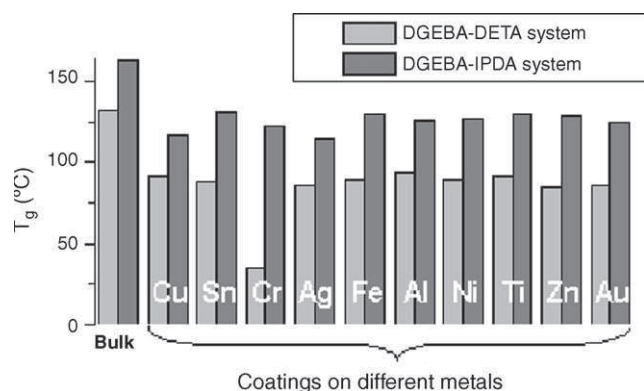


Fig. 7. Glass transition temperatures of pure and modified DGEBA-IPDA and DGEBA-DETA systems.

cis and *trans* isomers react with aluminium and form organo-metallic complexes [10]. The aluminium atoms could not be enumerated, as their concentration was too low, but wavelength dispersive spectroscopy (WDS) and energy dispersive spectroscopy (EDS) analyzes confirmed their presence inside the crystal.

3.3. New network formation

As mentioned in Section 3.1, the initial liquid epoxy-amine mixture was transformed into a mixture of organo-metallic complexes and pure (i.e., unmodified) amine with pure epoxy prepolymer. During the curing cycle, only non-crystallized organo-metallic complexes (leading to a new network having a lower T_g) and the pure amine (leading to the original epoxy network) can react with the epoxy monomer. We have already noticed that irrespective of the amine used (IPDA or DETA), coatings glass transition temperatures are lower than the pure bulk one, showing that both IPDA and DETA react with all the metals, including gold. Therefore, after reaction between the amine and the metallic surface, organo-metallic complexes are created, with a lower functionality than the pure amine functionality. Then, as the functionality of the amines decreased (but never dropped to zero) after their reaction with metallic ions, the amino groups are under the stoichiometric ratio in the interphase (even if initially the number of amino groups was equal to the number of epoxy groups) thus decreasing the glass transition temperature. This phenomenon was previously studied and described, by varying the initial stoichiometric ratio [19].

3.4. Discussion

When epoxy-amine prepolymers were applied onto metallic substrates, an interphase was created between the coating part having the bulk properties and the metallic

surface. The amine chemisorption on the metallic surfaces, concomitant with the partial dissolution of the surface oxide (and/or hydroxide) on the metal substrate was observed, according to the base character of amine monomers ($pK_a \geq 10$) and the acid character of the metals as shown by measuring their PZC (point of zero charge) [31]. Let us notice that hydroxides PZC are higher than oxides PZC [31], as the surface oxidation is very important for the amine chemisorption. Another parameter is the porosity of the surface layer: knowing the kind of hydroxide or oxide at the metallic substrate surface, both porosity and PZC can be found in literature. Finally, the viscosity of the polymer can increase (if it is low) or block (if the polymer is vitrified) the diffusion of the amine, and then its chemisorption.

Irrespective of the amine used, after their application onto the metallic surfaces, the amines (IPDA or DETA) were “modified” to form organo-metallic complexes. These complexes might crystallize if their solubility limit is exceeded. During the curing cycle, non-crystallized organo-metallic complexes reacted with the epoxy monomer leading to a new network.

Therefore, gold is able to react with the amines, as all the metals presented in this study, even if it is commonly known to be chemically inert since it is not covered by its oxidized form [1]. Indeed, gold corrosion was previously studied [32]; we have to remember that gold has a redox potential ($E_{Au/Au^{3+}}^\circ = 1.5$ V) and as a consequence can react with other chemical species [2–5,26,33,34]. In addition, this redox potential decreases a lot when gold complexes replace pure gold [26]. Now it is possible to interpret the amine-metal reaction as:

- An acid–base reaction between the amines and the metallic surfaces, leading to the organo-metallic complexes formation. In particular, it was shown that the amine forms a stable monolayer on the Au surface [33], using amine in liquid phase (as we did) as in vapour phase [35–38].
- After that, the complexes are easily oxidized (this is a redox reaction) leading to the dissolution of the first metallic layer. In particular, Greenwood and Earnshaw showed that the gold redox potential decreases a lot when gold complexes replace pure gold [26].

This hypothesis is supported by the coordination chemistry: it is well known that simple ligands such as amines bind more strongly to coordinatively-unsaturated metal centres [39]. As the amines are strong bases, they often bond to metals as two electron donors (instead of covalent bonds leading to amides formation). Then Venkataraman et al. [3] suggested that the bonding between Au and the amines is a simple delocalization of the lone pair of electrons from amine-nitrogen to coordinatively-unsaturated surface Au atoms.

Of course both acid–base and redox reactions depend on the metal, particularly in the case of gold which is not covered by its oxide or hydroxide. Then, the acid–base reaction depends on amine pK_a and surface PZC and the redox reaction depends on the standard reduction potential of the formed complex.

All these reactions are in competition with the polymerisation (i.e., epoxy-amine reaction): the acido-basic and redox reactions, and the ions or complex diffusion are misleading since the epoxy-amine system is vitrified.

4. Conclusions

We showed that all the mechanisms previously described [9,10,15,16,19] during the interphase formation can be observed irrespective of the metal used. All the metals were detected by ICP analyses in the metal-modified IPDA and DETA, and carbon peaks of modified DETA were shifted using ^{13}C NMR. Only modified IPDA (which reacted with the metals) crystallizes as sharp needles. Finally, irrespective of the metal and the amine used, coatings glass transition temperatures were lower than the one of pure bulk, showing that both IPDA and DETA react with all the metals, including gold.

So, gold reacts with the amines as the other metals and the amine-metal reaction can be described as the sum of acid-base and redox reactions (corresponding to the chemisorption of the amines on the metallic surfaces preceding the dissolution of the first metallic layer).

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