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Eprints ID: 5115

To link to this article: DOI:10.1016/j.ijadhadh.2006.09.009
<http://dx.doi.org/10.1016/j.ijadhadh.2006.09.009>

To cite this version:

Aufray, Maëlen and Alain André, Roche *Epoxy-amine/metal interphases: Influences from sharp needle-like crystal formation*. (2007) International Journal of Adhesion & Adhesives, vol. 27 (n° 5). pp. 387- 393. ISSN 0143-7496

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Epoxy–amine/metal interphases: Influences from sharp needle-like crystal formation

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Abstract

When epoxy–amine liquid mixtures are applied onto metallic oxide layer, concomitant amine chemical sorption and metallic surface dissolution appear leading to the organo-metallic complex formation. We studied the interphase formation and used two different amines as hardener (isophoronediamine (IPDA) and diethylenetriamine (DETA)). If the complex concentration within the liquid amine or epoxy–amine prepolymer is higher than its solubility limit, complexes crystallize. Sharp needle-like crystals are observed only with modified IPDA. For Al-IPDA crystals, the melting point is about 78 °C, but as the network is formed at this temperature, crystals remain present at the end of the polymerization cycle.

Keywords: Epoxy; Metals; Interphases; Crystal

1. Introduction

Epoxy–amine liquid prepolymers are extensively applied onto metallic substrates and cured to obtain painted materials or adhesively bonded structures. Overall performances of such systems depend on the substrate properties, the coating properties, and the created interphase between the organic layer and the substrate. When epoxy–amine liquid mixtures are applied onto metallic substrates (such as Al, Ti, Sn, Zn, Fe, Cr, Cu, Ag, Ni, Mg) or E-glass, amine chemical sorption concomitant with metallic surface dissolution appear, leading to the organo-metallic complex or chelate formation [1–8]. Furthermore, when the solubility is exceeded and the complex geometry makes their crystallization possible, organo-metallic complexes may crystallize. These crystals induce changes of mechanical properties (effective Young's modulus, residual stresses, practical adhesion, durability [9–16]). Some studies report the influence of the metallic substrate nature on the coating-substrate adhesion [17], but the interphase formation

depends on many other parameters, such as hardener nature, curing cycle, viscosity of the prepolymer mixture.

In this work, two different amines were used and mixed to the diglycidyl ether of bisphenol A (DGEBA) epoxy monomer ($a/e = \text{aminohydrogen function/epoxy function} = \text{stoichiometric ratio} = 1$) to form bulk materials or coatings. The IPDA (IsoPhoroneDiAmine) is a cycloaliphatic diamine which may crystallize after modification (i.e. after being applied onto the metal surface leading to a chemical reaction between the liquid amine and the metal), whereas the diethylenetriamine (DETA) is an aliphatic triamine. The modified DETA never crystallizes, even after 3 h in contact with aluminum. We evaluated parameters determining interphase formation, and some properties of the Al-IPDA crystals (i.e. IPDA reacted with the aluminum and crystallized), for example their melting point. Finally, we correlated the results to the change of mechanical properties observed by many authors [5,6,9–16].

2. Experimental

2.1. Materials

The metallic substrates used were 1.200 ± 0.005 mm thick 1050 (0.25% Si, 0.4% Fe, 0.05% Cu, 0.05% Mn,

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0.05% Mg, 0.05% Zn, 0.03% Ti, 0.05% V, i.e. min. 99.5% Al) commercial aluminum alloys from P echiney. Aluminum sheets were prepared by die-cutting to provide identical sized strips ($50 \times 10 \text{ mm}^2$). Before any polymer application, aluminum substrate surfaces were ultrasonically immersed in acetone for 10 min, wiped dry, 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 aluminum sulfate octadecahydrate) for 1 h at 60°C , and rinsed in running water for 1 min. Then, they were plunged into deionized water for 5 min and they were wiped dry.

After the surface treatment, all substrates were stored less than 2 h in an air-conditioned room ($20 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ rh) before polymer application. The DGEBA (MW = 348 g mol^{-1} , DGEBA DER 332 from Dow Chemical) was used as epoxy prepolymer and the curing agents were either IPDA from Fluka or DETA 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. According to Montois [13,14], we studied the influence of the initial epoxy-amine mixture viscosity on the interphase formation. In order to have various initial viscosities, a mixture of DGEBA DER 332 and DER 671 was made at 100°C .

To control the extent of chemical reactions between the metallic surface and the liquid monomers, that lead to the formation of a more or less thick interphase, the liquid epoxy-amine mixtures were kept in contact with the metallic surface at room temperature for various periods of time (from 1 min to 3 h) before starting the desired adhesive curing cycle (e.g. see Fig. 1). Conversely, when the interphase formation was not desired, coated specimens were placed in the preheated oven right after the epoxy-amine application (i.e. within less than 1 min). These curing cycles allowed the maximum conversion (i.e. the maximum glass transition temperature). It is important to notice that the DGEBA-DETA system is vitrified in less than 1 h at room temperature. Consequently, the interphase formation stops as soon as the system is vitrified and the interphase properties are expected to remain constant

after 1 h at room temperature. At high temperature, vitrification appears within a few minutes, stopping any reaction between the amine and the metal, and/or diffusion phenomenon.

2.2. Infra-red spectroscopy (μFTIR)

Micro-IR map was made using FTIR Imaging Spotlight 300 from Perkin-ElmerTM. To determine the practical adhesion, thick stiffeners ($25 \times 5 \times 4 \text{ mm}^3$) made of polymer were mold onto the metallic substrate and debonded by mechanical testing with a three-point flexure test (ISO 14679). After this test, it was possible to cut 1 mm thick slices of the polymer (perpendicularly to the adherent surface) and to analyze them. A transmission infra-red map could be realized, data points being collected every $6 \mu\text{m}$ stage sample displacement along a line perpendicular to the metal surface. According to the D66545 Perkin-Elmer Product Note, the dual imaging resolution was $6.25 \mu\text{m}$ per pixel. Infra-red spectra were recorded in the $3000\text{--}7800 \text{ cm}^{-1}$ range using a dual mode detector and imaging mode was used. For each analysis, 16 scans were collected at 16 cm^{-1} resolution.

2.3. Inductively coupled plasma spectroscopy (ICP)

An ICP spectrometer (simultaneous VISTA from VARIAN) was used with a 40 MHz generator and a new CCD detector (70,908 pixels, wavelength from 167–785 nm) to determine the metal ion concentration within the liquid amine after a 3 h liquid/solid contact time. Distilled water was used as the diluting agent (each sample—from 1–10 mg—was diluted in 50 ml of distilled water).

2.4. X-ray diffraction (XRD)

The structural studies of the organo-metallic crystals had been conducted at room temperature by XRD. It was necessary to increase their size, considering their initial shape (sharp needles) and dimensions ($1 \mu\text{m}$ in diameter and $50 \mu\text{m}$ long). Therefore, they were dissolved in deionized water and after a very slow water evaporation process, the organo-metallic complexes re-crystallized. The shape factor was identical, but they became bigger (about 1 mm long). As they were single crystals (extinction observed using polarized optical microscopy—POM), they could be analyzed by XRD. Single-crystal diffraction data were collected using a Nonius Kappa CCD diffractometer.

2.5. POM coupled with a hot stage apparatus

Crystallized complexes or epoxy-modified amine mixtures could be melted or cured between two glass plates using a Mettler FP 82 hot stage, coupled with a FP 90 central processor, under POM (Laborlux 12POLs from Leica equipped with a CCD-IRIS color video camera from

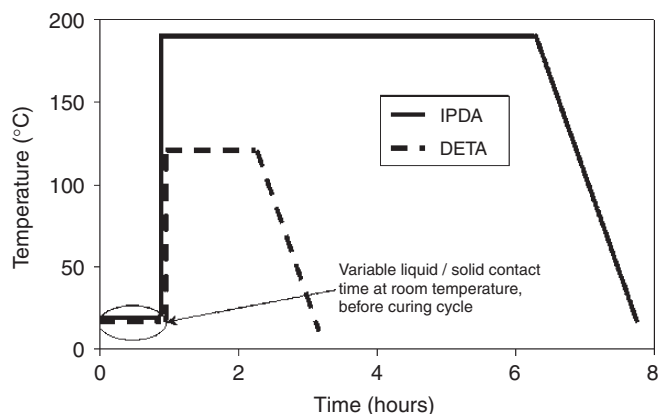


Fig. 1. Curing cycles for DGEBA-IPDA and DGEBA-DETA systems.

Sony). Crystals were heated from 25 to 100 °C at a rate of 1 K min⁻¹ and the mixtures were cured from 20 to 250 °C (see Section 3.4).

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 [15,16], we had already shown that the interphase formation mechanisms was a result of the dissolution of the metallic surface layers, concomitant with the ion diffusion through the liquid prepolymer. In order to detect the dissolution phenomenon, pure amine (either DETA or IPDA) was previously applied onto chemically etched metallic sheets. After 3 h, the metallic surfaces were scraped with a PTFE spatula. The “modified” amine (i. e. the amine reacted with the metal) was analyzed. Whatever the amine and the metal natures were, metal ions were detected in the “modified” amines by ICP analysis and new peaks were detected by infra-red spectroscopy. To verify the hydroxide dissolution, a very thin layer of liquid IPDA was applied onto chemically etched aluminum, and IRRAS spectra were made every 5 min (hydroxide band intensity variation at ≈ 3430 cm⁻¹ was followed). Hydroxide group peak intensity decreased when the amine/metal contact time increased. Conversely, if pure DGEBA monomer was applied onto the aluminum surface, even after 3 h in contact with the metallic surface, no metal ion was detected by ICP in the recuperated DGEBA and the

infra-red spectra remained identical, before and after the contact with the metal.

The amine chemisorption on oxidized or hydrated and oxidized metal surfaces, concomitant with the partial dissolution of the surface oxide (and/or hydrated and oxidized) 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 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 metallic surfaces, both amines were modified to form an organo-metallic complex. Then, 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.

To determine the practical adhesion, a 4–5 mm thick polymer block was molded onto the metallic substrate and the cured polymer stiffener was debonded during mechanical test (ISO 14679). To verify that the interphase formation mechanisms took place either in coatings or volumes, it was possible to slice (perpendicular to the surface of the adherent) and to analyze the epoxy–amine polymer block, after the three-point flexure test. Then, a transmission infra-red map could be realized, where we considered the 4530 cm⁻¹ band (epoxy combination band), the 6500 cm⁻¹ band (amine band), and the 4623 cm⁻¹ band (aromatic C–H ring stretch combination band, used as a reference). The normalized amine and epoxy band intensity

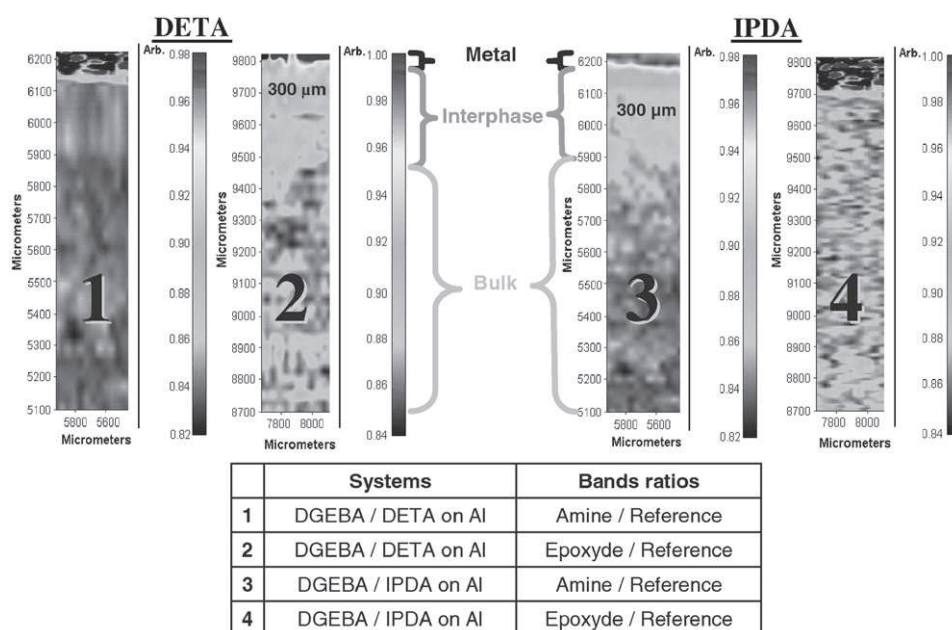


Fig. 2. Micro-FTIR map of the interphase for DGEBA–IPDA and DGEBA–DETA systems.

variations were derived from μ -IR spectroscopy for DGEBA/IPDA or DETA systems (e.g. see Fig. 2). The top of the sample was initially in contact with the metal. It is important to notice that both normalized amine band intensity for DETA system and normalized epoxy band intensity for IPDA system remained quite constant whatever the thickness was, as represented on the maps 1 and 4 of Fig. 2. On the maps 2 and 3, an interphase (corresponding to the region where band ratios vary), and a bulk (with homogenous properties) were observed. The interphase thickness is about 300 μm for both IPDA and DETA systems.

Finally, we evaluated the interphase thickness versus liquid/solid contact time at room temperature (e.g. see Fig. 3) and viscosity of the prepolymer mixtures (e.g. see Fig. 4). Whatever the nature of the amine was, the interphase thickness increased when the liquid/solid contact time at room temperature increased (e.g. see Fig. 3). Moreover, the interphase thickness decreased when the viscosity of the prepolymers mixtures increased (e.g. see Fig. 4). When a liquid prepolymer mixture was applied at room temperature onto a metallic surface, there was a competition between the epoxy-amine polymerisation, and

the organo-metallic complexes formation. The low temperatures favored the organo-metallic complexes formation, whereas the high temperatures (curing temperatures, presented on the Fig. 1) favored epoxy-amine polymerization. As a consequence, the longer the liquid/solid contact time was at room temperature, the thicker was the interphase. Moreover, the low viscosity favored the diffusion of metallic ions and/or organo-metallic complexes, and consequently, favored the growth of the interphase as shown in Fig. 4.

3.2. New network formation

During the curing cycle, only non-crystallized organo-metallic complexes can react with the epoxy monomer leading to a new network having a lower T_g . We have already noticed that whatever the amine (IPDA or DETA) and the metal were, coatings glass transition temperatures were lower than the pure bulk T_g [15,16], and previously described mechanisms were also observed for any metallic substrates provided they were covered by an oxide or hydroxide layer.

3.3. Crystallization of "modified" IPDA

If the complex (or chelate) concentration within the liquid amine or epoxy-amine prepolymer is higher than its solubility limit, and the complex geometry makes their crystallization possible, organo-metallic complexes may crystallize. Sharp needle-like crystals were observed with modified IPDA whatever the metal nature was, whereas modified DETA never crystallized (even after 3 h in contact with any metal). Considering their initial dimensions, it was necessary to increase their size. Therefore, the organo-metallic complexes were recrystallized. Fig. 5 represented the recrystallized crystals observed by eyes and Fig. 6

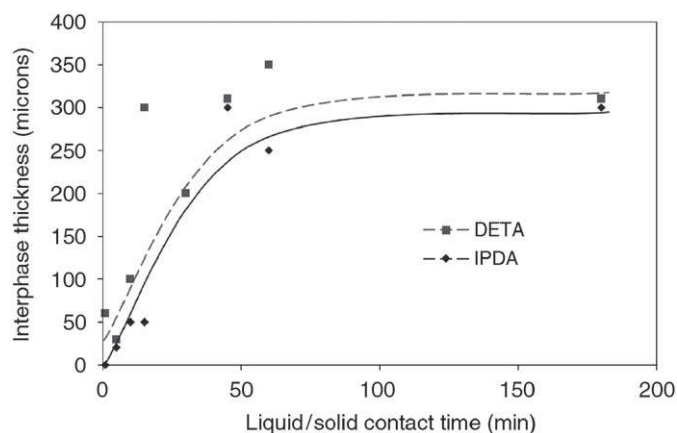


Fig. 3. Interphase thickness versus liquid/solid contact time at room temperature.

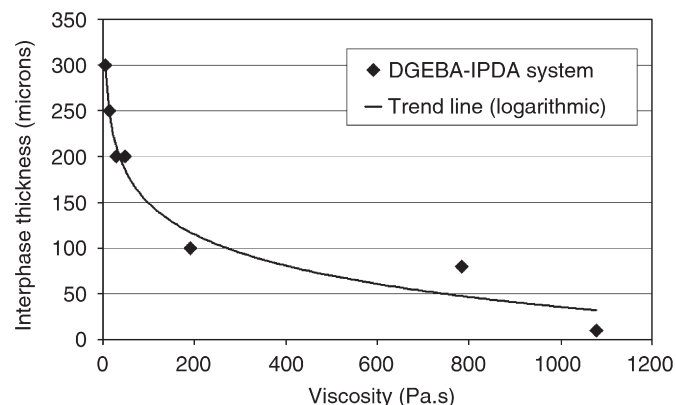


Fig. 4. Interphase thickness versus viscosity of the prepolymers mixtures.

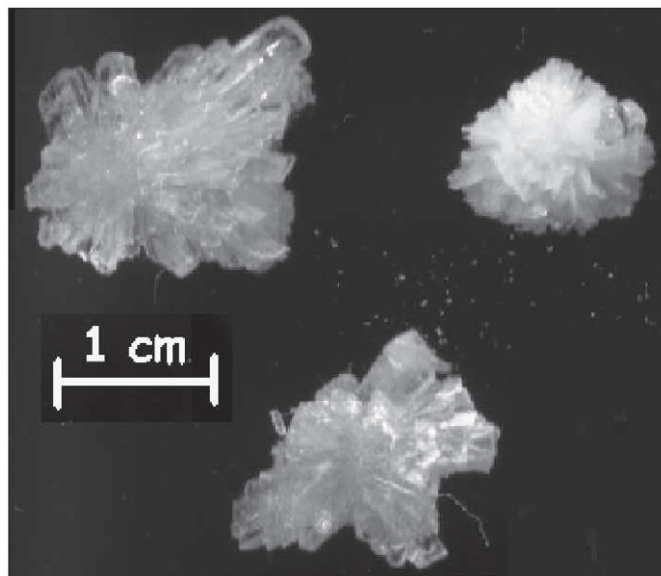


Fig. 5. IPDA-Al crystals observed by eyes.

represented the same crystals observed by SEM. Unfortunately, IPDA became solid after reaction with the air, even without any contact with a metal surface. Therefore, the IPDA could react with air carbon dioxide and form carbonates, but it was possible to distinguish organo-metallic crystals to IPDA carbonates, as the organo-metallic crystals looked like sharp needle and the carbonates were fluffy. To determine the crystal melting temperature, they were melted under POM (e.g. see Fig. 7).

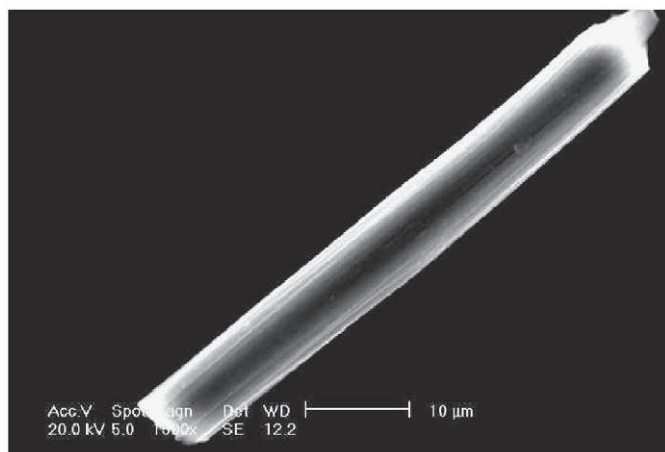


Fig. 6. IPDA-Al crystals observed SEM.

For Al-IPDA crystals, the melting point was in the range 75–80 °C (e.g. see Fig. 7), whereas carbonated IPDA became liquid at 87 °C. In addition, the observed crystals were single crystals (extinction was observed using POM) whereas the carbonates were simply in a solid state (extinction was not observed using POM). Then, Al-IPDA crystals were analyzed by XRD. The unit cell was represented in Fig. 8. We could recognize the IPDA, 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. The aluminum atom was not represented, as its concentration was too low, but wavelength dispersive spectroscopy (WDS) and energy dispersive spectroscopy (EDS) analyzes confirmed its presence inside the crystal. Only the *trans* isomer crystallize after modification by aluminum (no *cis* isomer was observed by XRD), even if both *cis* and *trans* isomers react with aluminum and form organo-metallic complexes [4]. On the right of Fig. 8, crystal packing was represented with unit cell parameter: Al-IPDA crystallized in a monoclinic system and the space group was Pc.

Bentadjine and Debontridder [5,6] have previously found a mechanism to explain the chelate formation using ethlenediamine (DAE) (i.e. the chemical reaction leading to organometallics, e.g. see Fig. 9). The chemical reaction

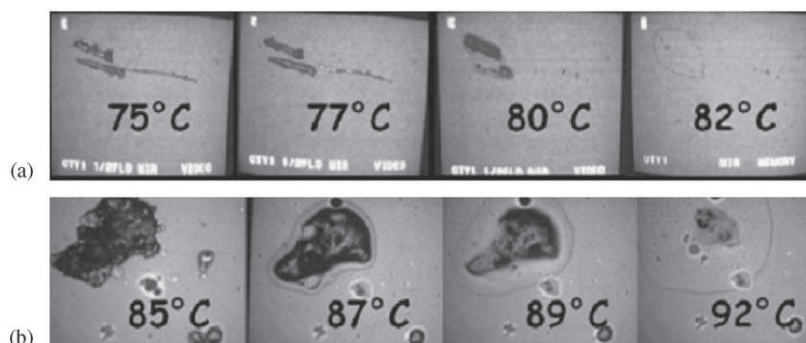


Fig. 7. Hot stage microscopy of IPDA-Al crystals and carbonated IPDA.

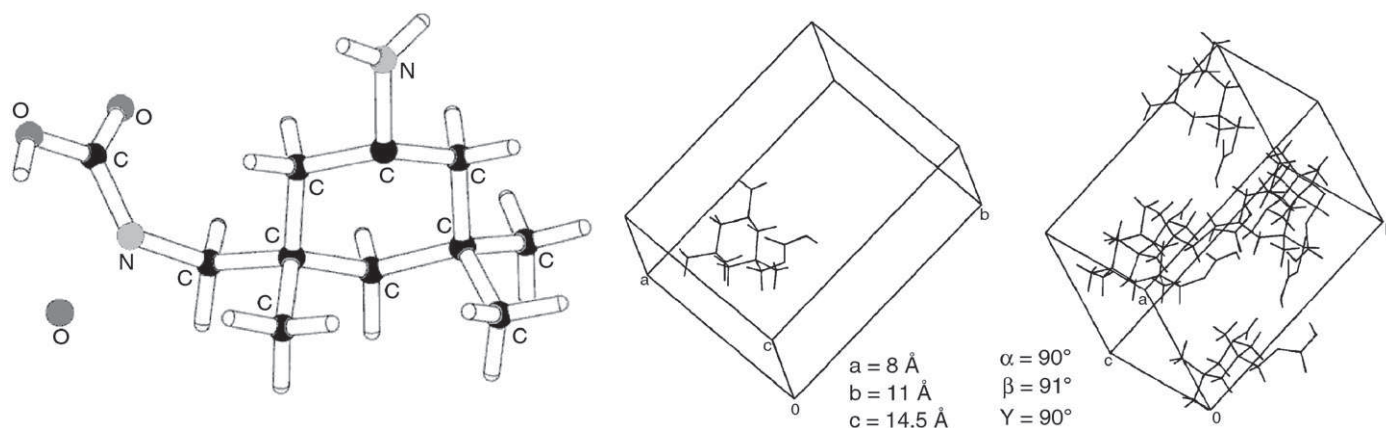


Fig. 8. IPDA-Al crystalline structures: unit cell of crystals (on the left), and crystal packing (on the right).

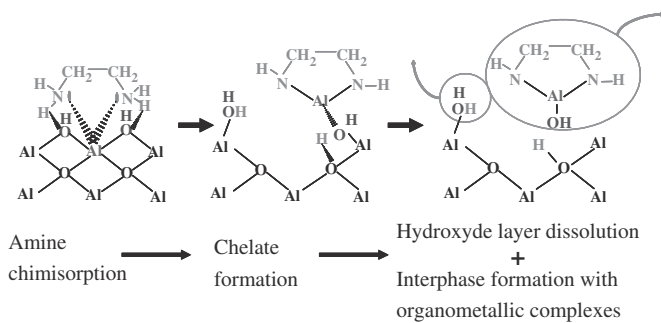


Fig. 9. Organometallic interphase formation (from [5,6]).

leading to the Al-IPDA could be the same one, even it was not represented here for the sake of simplicity. We could nevertheless add that Al-IPDA needed both water and carbon dioxide to crystallize, as seen in this section. Some ICP was investigated on the recrystallized Al-IPDA crystals (i.e. only crystals, without liquid pure or modified IPDA). Fig. 9 could be misleading as there were some pure IPDA in the Al-IPDA crystals: crystals were made of about 30 IPDA molecules for only one aluminum atom (and water and carbon dioxide, as shown before).

3.4. Heat performance of the crystals

We had already mentioned that the crystal melting point was around 80 °C (see Section 3.3). But the highest temperature of the DGEBA-IPDA curing cycle was 190 °C (e.g. see Fig. 1), and we firstly mentioned that these crystals induced changes of mechanical properties, such as Young's modulus, residual stresses, practical adhesion, and durability (Section 1). In order to verify the presence of crystals within the cured material, even after the entire curing cycle (so they could act as short fibers after cooling down), we followed, using POM, their behavior during the DGEBA "modified" IPDA curing cycle (e.g. see Fig. 10). Whatever the temperature was, needle-like shapes (like our initial organo-metallic crystals) could be observed. For our DGEBA-IPDA pure prepolymer mixtures, the vitrification temperature was 60 °C. The DGEBA-IPDA system vitrified before the melting temperature (80 °C) of crystals. For temperatures higher than 60 °C, even if organo-metallic complexes were melted (i.e. liquid), they remained trapped within the vitrified matrix. Vitrified polymer and melting crystals' refractive index being different, the interface formed between the liquid phase of the organo-metallic complex and the vitrified matrix could be observed during the full curing cycle. After the cooling down, in Fig. 10, we did not know if the observed shapes showed any re-crystallization of complexes or the presence of organo-metallic complexes remaining in their liquid state. However, according to their shape factor and their orientation (parallel to the metallic surface), only crystals' could act as short fibers in matrix and modify the polymer mechanical properties, as described in previous works [9,10,15]. For 100 μm thick coatings, longitudinal Young's

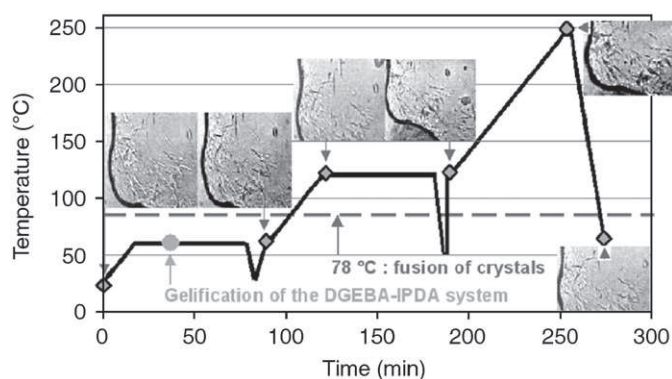


Fig. 10. Heat performance of the Al-IPDA crystals during the DGEBA-IPDA curing cycle.

module were determined (using three point flexure test) and found to be 5 and 2 GPa for DGEBA-IPDA and DGEBA-DETA coatings, respectively. For relevant bulk materials, their Young's moduli were about 3 GPa. Let us not forget that crystals were found only using IPDA hardener, so the increase of Young's modulus could be associated to the crystal formation and orientation.

4. Conclusion

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 ($pK_a \geq 10$). Then it could be assumed that either:

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

Whatever the amines were, after application onto metallic surfaces, they were "modified" to form organo-metallic complexes. These complexes might crystallize if their solubility limit was exceeded. During the curing cycle, non-crystallized organo-metallic complexes reacted with the epoxy monomer leading to a new network. For Al-IPDA crystals, the melting point was in the range 75-80 °C. Al-IPDA crystallized in the monoclinic system and their space group was Pc. The amine may also react with carbon dioxide to form carbonates. Their melting points were determined to be about 87 °C. Finally, organo-metallic crystals looked like sharp needle and carbonates were fluffy, therefore, we are now able to differentiate both the compounds, the carbonates and the organo-metallic

complexes. Finally, these needle-like structures were observed during the curing cycle. They modify the polymer mechanical properties by acting as short fibers, and even if crystals melted at 80 °C, they remained embedded into the vitrified polymer.

Acknowledgments

We acknowledge the crystallographic group of Claude Bernard University from Lyon1 (mainly D. Merle, Prof. Perrin and Dr. Thozet) for doing XRD analyses and for their helpful discussion.

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