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Properties of the Interphase Epoxy–Amine/Metal: Influences from the Nature of the Amine and the Metal

M. Aufray and A. A. Roche

Abstract

Epoxy–amine systems are used as adhesives and paints in many industrial applications. When they were applied on metallic substrates and cured, an interphase was created between the substrate and the polymer. The interphase had chemical, physical and mechanical properties, different than the bulk phase. Amines are known to chemically react with metallic ions to form organometallic complexes. Two amines were used: the diethylenetriamine (DETA) and the isophorone diamine (IPDA). When the IPDA organometallic complexes were over the solubility limit, chelates crystallized, whereas for DETA, organometallic complexes were formed but never crystallized. The crystals were analysed. For Al-IPDA crystals, the melting point was in the range of 75–80 °C. The new mechanical properties came from the crystals, that remained enclosed within the vitrified polymer; this was due to the crystals melting point, which was higher than the DGEBA-IPDA systems vitrification temperature.

7.1

Introduction

Epoxy–amine liquid prepolymers are extensively applied to metallic substrates and cured to obtain painted materials or adhesively bonded structures. Overall performances of such systems depend on the interphase created between the organic layer and the substrates. When epoxy–amine liquid mixtures are applied to a more or hydrated metallic oxide layer (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 organometallic complex or chelate formation [1, 2]. Furthermore, when the solubility product is exceeded, organometallic complexes may crystallize. These crystals induce changes of mechanical properties (effective Young's modulus, residual stresses, practical adhesion, durability, etc.).

In this work, two different amines were used and mixed with 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 to the metal surface, leading to chemical reaction between liquid amine and metal), whereas the DETA (diethylenetriamine) is an aliphatic triamine which never crystallizes, even after 3 h in contact with aluminum. We evaluated some properties of the IPDA crystals (i.e., IPDA reacted with the metal, and crystallized), such as their melting point, and correlated the results with the change in mechanical properties. Finally, we studied the influence of the stoichiometric ratio a/e on the polymerization of our systems.

7.2

Materials and Methods

7.2.1

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, 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 identically sized strips (50×10 mm²). Before any polymer application, aluminum substrate surfaces were cleaned by ultrasonic immersion in acetone for 10 min, wiped dry, submerged in a sulfochromic 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) 1 h at 60 °C, rinsed in running water for 1 min, allowed to stand in deionized water for 5 min and wiped dry.

After surface treatment, all substrates were stored less than 2 hours in an air-conditioned room (20 ± 2 °C and $50 \pm 5\%$ r.h.), before polymer application. The epoxy prepolymer used was diglycidyl ether of bisphenol A (MW=348 g mol⁻¹, DGEBA DER 332 from Dow Chemical). 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 used was equal to 1 (exceptions are mentioned).

To control the extent of chemical reactions between the metallic surface and liquid monomers, leading to the formation of a thick interphase, liquid epoxy-amine mixtures were kept in contact with the metallic surface at room temperature for various periods of time before the desired adhesive curing cycle was started (e.g., see Fig. 7.1): at 190 °C, vitrification appeared within a few minutes, stopping any reaction between amine and metal, and/or diffusion phenomenon. These curing cycles allowed the maximum conversion (i.e., the maximum glass transition temperature). Conversely, when interphase formation was not desired,

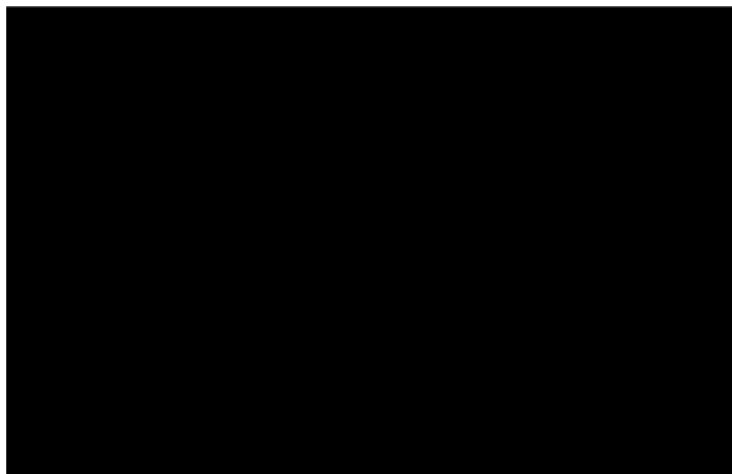


Fig. 7.1 Curing cycles of the DGEBA–IPDA and DGEBA–DETA systems.

coated specimens were placed in the preheated oven immediately after the epoxy–amine application (i.e., within less than 1 min).

7.2.2

Thermal Analysis (DSC)

Differential scanning calorimetry (DSC) experiments were carried out in a Mettler (DSC 30) apparatus to determine the onset glass transition temperature ($T_{g \text{ onset}}$) 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 K min^{-1} under a continuous flow of U-grade argon. Samples were weighed using a Mettler balance having a $\pm 5 \mu\text{g}$ sensitivity. The calorimeter was calibrated with both indium and zinc. The glass transition temperature was determined with $\pm 1 \text{ K}$ accuracy.

7.2.3

Micro-Infrared spectroscopy (μ -FTIR)

“Micro-IR” maps were 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 molded 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 polymer (perpendicularly to the adherend surface) and to analyze them. A transmission infrared map could be realized, data points being collected at every $6 \mu\text{m}$ interval of sample displacement along a line perpendicular to the metal surface. According to the D66545 Perkin-ElmerTM Product Note, the dual imaging resolution was $6.25 \mu\text{m}$ pixel size. Infrared spectra were recorded in the $3000\text{--}7800 \text{ cm}^{-1}$ range using a dual-mode

detector. The imaging mode was used. For each analysis, 128 scans were collected at 4 cm^{-1} resolution.

7.2.4

Fourier Transform Near-Infrared Spectroscopy (FT-NIR)

A near-infrared spectrometer (Equinox 55 from Bruker) was used with OPUS software. The near-infrared spectra were recorded in the $4000\text{--}8000\text{ cm}^{-1}$ range. For transmission analysis, polymer coatings (from $50\text{ }\mu\text{m}$ to 2 mm thick) were analyzed after debonding of the coating from the substrate by bending the coated substrate, and background spectra in air were recorded. For each analysis, 128 scans were collected at 4 cm^{-1} resolution.

7.2.5

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 to 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 to 10 mg – was diluted in 50 mL of distilled water).

7.2.6

X-Ray Diffraction (XRD)

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

7.2.7

Polarized Optical Microscopy (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 an FP 90 central processor, under POM (Laborlux 12POLS from Leica, equipped with a CCD IRIS color video camera from Sony). Crystals were heated from 25 to $100\text{ }^\circ\text{C}$ at a rate of 1 K min^{-1} and mixtures were cured from 20 to $250\text{ }^\circ\text{C}$ (see Section 7.3.4).

7.3

Results and Discussion

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

7.3.1

Interphase Formation Mechanisms

In previous studies [3, 4], we had pointed out that the interphase formation mechanisms result from dissolution of the metallic surface layers, concomitantly with ion diffusion through the liquid prepolymer. In order to detect the dissolution phenomenon, pure amine (either DETA or IPDA) was previously applied to chemically etched metallic sheets (either Al or Ti alloys were used, and had hydroxidic surfaces). 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 natures of the amine and the metal were, metal ions were detected in the “modified” amines by ICP analysis and new peaks were detected by infrared spectroscopy [5]. To indicate hydroxide dissolution, a very thin layer of liquid amine was applied to chemically etched aluminum, and Infrared Reflection – Absorption Spectroscopy (IRRAS) spectra were recorded every 5 min (the hydroxide band intensity variation at ca. 3430 cm^{-1} was followed). The OH group peak intensity decreased when the amine–metal contact time increased [5]. Conversely, if pure DGEBA monomer was applied to the metal surfaces, even after 3 h in contact with the metallic surfaces, no metal ion was detected by ICP in the DGEBA recovered, and the infrared spectra remained identical before and after the contact with the metal. Finally, if pure amine monomer was applied to gold-coated substrates, no chemical reaction was observed (by either ICP or FTIR analyses).

The amine chemisorption onto oxidized or hydroxidized metal surfaces, concomitantly with the partial dissolution of the surface oxide (and/or hydroxide) metal substrate, was observed according to the fact that amine monomers are basic. 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 organometallic complexes, or
- organometallic complexes form on the metal surface layer [6] and diffuse within the liquid monomer mixture (epoxy–amine).

For all systems except those on gold, after application to metallic surfaces amines were modified to form an organometallic complex. Then, the initial liquid epoxy–amine mixture was transformed into a mixture of organometallic complexes and pure (i.e., unmodified) amine with pure epoxy prepolymer.

7.3.2

Formation of New Networks

During the curing cycle, only uncrystallized organometallic complexes can react with the epoxy monomer, leading to a new network having a lower T_g . Previously, the presence of the two networks (the initial one and the “modified” one) was revealed by DSC and DMTA [3]. In order to detect modification of the network, some coatings were made on various kinds of substrate (Al, Ti, Sn, Zn, Fe, Cr, Cu, Ag, Ni, Mg, Au, and E-glass) covered by their natural oxide layer. Curing took place on the metals and on the E-glass. Then the coated substrates were bent to pull off the coating layer. The glass transition temperature could easily be determined for such free coatings. The relevant glass transition temperatures of coatings were compared with the bulk data (e.g., see Table 7.1). Whatever the amine (IPDA or DETA) and the metal were, the glass transition temperatures of the coatings were lower than that of the pure bulk T_g (except with a gold substrate). So, the mechanisms described previously were also observed for any metallic substrates provided they were covered by an oxide or hydroxide layer.

7.3.3

Crystallization of “Modified” IPDA

If the complex (or chelate) concentration within the liquid amine or epoxy-amine prepolymer was higher than its solubility limit, complexes (or chelates) crystallized. Sharp needle-like crystals were observed with modified IPDA what-

Table 7.1 Influence of the nature of the amine and the metal on the glass transition temperature T_g of coatings.

Metal	T_g [°C]	
	DETA	IPDA
Bulk	132	163
Cu	92	117
Sn	88	131
Cr	35	122
Ag	86	114
Si	91	129
Fe	89	130
Al 5182	94	115
Al 1050	94	126
Ni	89	127
Ti	91	130
Zn	85	129
Mg	76	128
Au	132	163

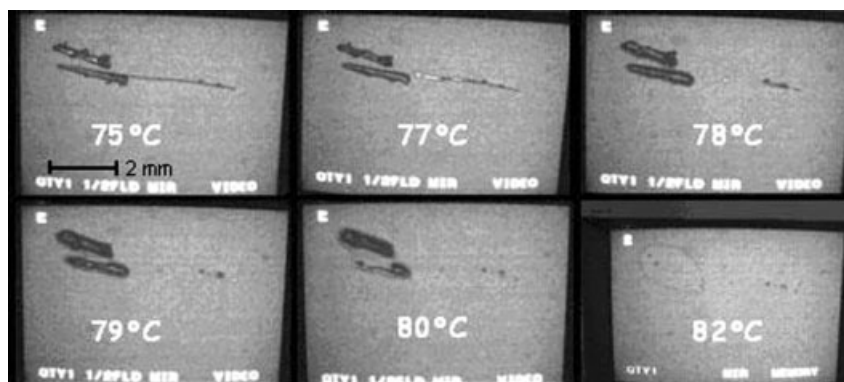


Fig. 7.2 Series of POM images showing determination of the melting point of crystals.

ever the nature of the metal (except gold), whereas DETA never crystallized (even after 3 h in contact with any metal). Considering their initial dimensions, it was necessary to increase their size. The organometallic complexes were therefore recrystallized. Then, crystals could be melted under POM (e.g., see Fig. 7.2) to determine their melting temperature and to observe, or not, extinction under polarized light. For Al-IPDA crystals, the melting point was in the range 75–80°C, and the crystals observed were single crystals (extinction was observed using POM). They were analyzed by XRD and seemed to be orthorhombic ($\alpha = \beta = \gamma = 90^\circ$).

7.3.4

Modification of Mechanical Properties

We have mentioned that the crystal melting point was around 80°C (see Section 7.3.3), but the highest temperature of the DGEBA-IPDA curing cycle was 190°C (e.g., see Fig. 7.1), and we firstly mentioned that these crystals induced changes of mechanical properties, such as Young's modulus, residual stresses, practical adhesion, and durability [7] (Section 7.1). In order to confirm the presence of crystals within the cured material, even after the entire curing cycle (so that they could act as short fibers after cooling), we followed their behavior during the DGEBA-“modified” IPDA curing cycle, using POM (e.g., see Fig. 7.3). Whatever the temperature was, needle-like shapes (like our initial organometallic crystals) could be observed. For our DGEBA-IPDA pure prepolymer mixtures, the vitrification temperature was 60°C [3], so this DGEBA-IPDA system vitrified before the melting temperature (80°C) of the crystals. For temperatures higher than 60°C, even if organometallic complexes were melted (i.e., liquid), they remained trapped within the vitrified matrix. As the refractive indices of the vitrified polymer and the melting crystals were different, the interface formed between the liquid phase of the organometallic complex and the vitrified

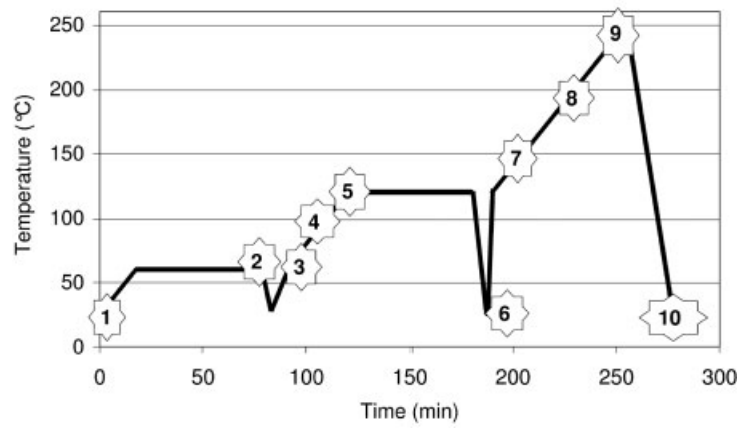
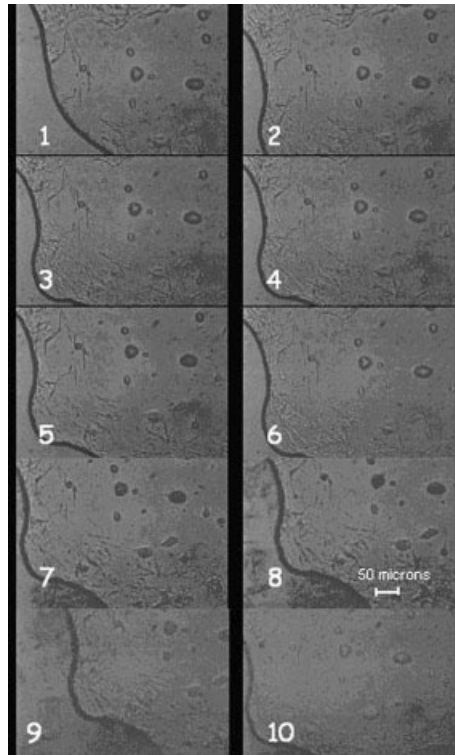


Fig. 7.3 Series of POM images showing evolution during a DGEBA/Al-modified IPDA curing cycle.

matrix could be observed during the full curing cycle. After the cooling down (Fig. 7.3, POM image 10), we were unable to tell whether the observed shapes showed any recrystallization of complexes or the presence of organometallic 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 the matrix and modify the polymer's mechanical properties, as described in previous work [7]. For coatings 100 μm thick, longitudinal Young's moduli were determined (using the three-point flexure test [8]) and found to be 5 and 2 GPa for DGEBA-IPDA and DGEBA-DETA coatings respectively. The Young's moduli of the relevant bulk materials were about 3 GPa. As crystals were found only when IPDA hardener was used, the increase in Young's modulus could be associated with the crystal formation and orientation [9].

7.3.5

Comparison of Coatings and Metal-Bulk Interphases

To determine the practical adhesion, a polymer block 4–5 mm thick was molded onto the metallic substrate. The cured polymer stiffener was debonded during the mechanical test (ISO 14679). To verify that the interphase formation mechanisms took place either in the coatings or in the bulk, after the three point flexure test it was possible to slice the epoxy-amine polymer block (perpendicular to the surface of the adherend) and to analyze it. Then, a transmission infrared map could be realized. We considered the bands at 4530 cm^{-1} (epoxy combination), 6500 cm^{-1} (amine), and 4623 cm^{-1} (the aromatic C-H ring stretch combination, used as the reference) [2]. Normalized amine and epoxy band intensity variations are derived from μ -FTIR spectroscopy for DGEBA-IPDA or DGEBA-DETA systems (e.g., see Fig. 7.4). The normalized amine band intensity variations are given for the IPDA system, whereas the normalized epoxy band intensity variations are shown for the DETA system. Both the normalized amine band intensity for the DETA system and the normalized epoxy band intensity for the IPDA system remained quite constant whatever the thickness, and were not represented. The top of the sample was initially in contact with the metal. On both maps, an interphase (corresponding to the region where band ratios vary), and a bulk region (with homogenous properties) were observed. The interphase thickness is about 300 μm for IPDA systems and 500 μm for DETA systems. In order to determine whether coatings and bulk materials behave identically near the metal surfaces, the μ -FTIR analyses for polymer slices were compared with FT-NIR data from coatings of varying thickness. Amine (χ_a) and epoxy (χ_e) degrees of conversion were calculated, using the ratio of the respective band areas, by Eq. (1).

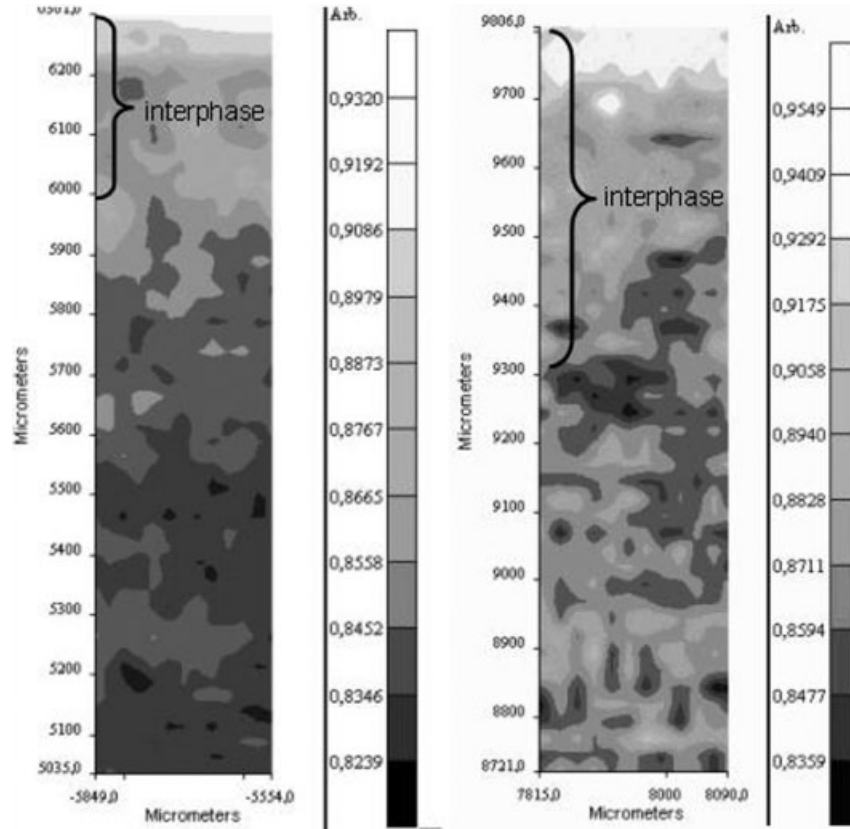


Fig. 7.4 Micro-FTIR map of the interphase for DGEBA–IPDA (left) and DGEBA–DETA systems (right).

$$\chi_{e(\text{NIR})} = 1 - \frac{\left(\frac{A_{4530}}{A_{4623}}\right)_t}{\left(\frac{A_{4530}}{A_{4623}}\right)_{t=0}} \quad \chi_{a(\text{NIR})} = 1 - \frac{\left(\frac{A_{6500}}{A_{4623}}\right)_t}{\left(\frac{A_{6500}}{A_{4623}}\right)_{t=0}} \quad (1)$$

χ_a and χ_e were determined for both systems (initially DGEBA–IPDA and DGEBA–DETA were mixed in the stoichiometric ratio ($a/e=1$), then they were applied to the metal surface and state 3 had room temperature before the curing cycle was started) and photographed (e.g., see Fig. 7.5): χ_a for DETA and χ_e for IPDA were quite constant and equal to 1, whatever the coating thickness. In addition, as observed by μ -IR spectroscopy (e.g., see Fig. 7.4), χ_a decreased near the metallic surface for the IPDA, while χ_e decreased near the metallic surface for the DETA system. The only difference between the two systems was the crystallization of organometallic complexes for the IPDA system, whereas DETA complexes never crystallized. Whatever the amine was (either IPDA or DETA),

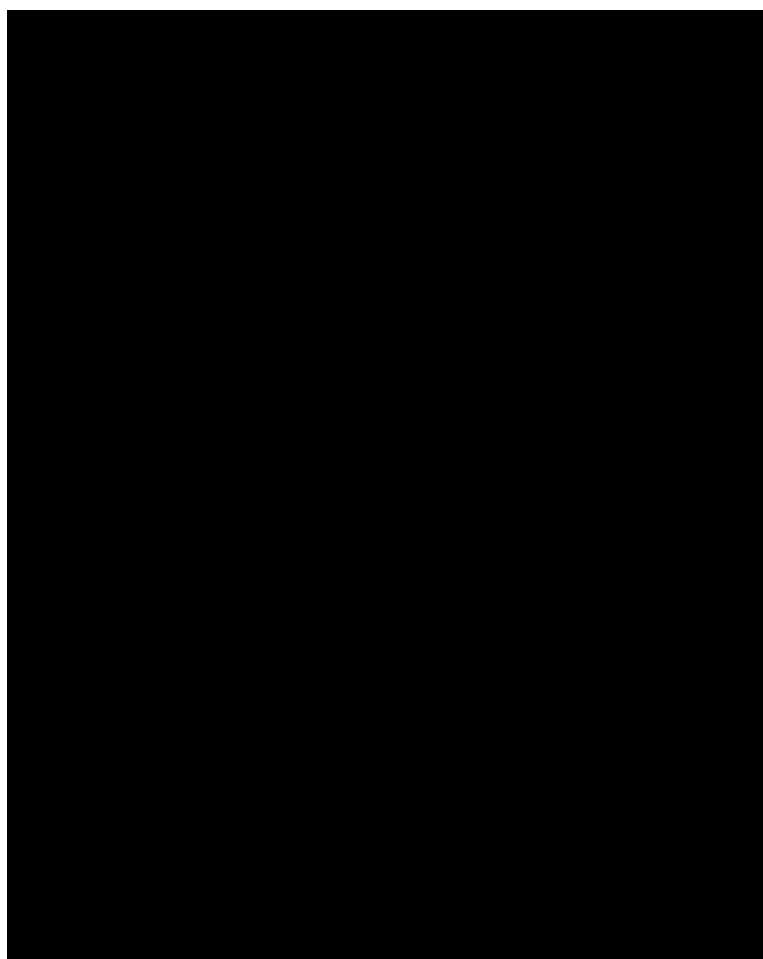


Fig. 7.5 Degrees of conversion for amine (χ_a) and epoxy groups (χ_e) versus coating thickness by NIR spectroscopy.

modified and unmodified amines had very similar NIR spectra [3]. In particular, we could find the same amine band at 6500 cm^{-1} . Indeed, when modified IPDA crystallized, modified amines within the crystal phase could not react with epoxy groups, so unreacted amino groups were detected by NIR. In addition, epoxy groups might react together by an etherification reaction [3, 10] during curing, catalyzed by metallic ions. Consequently, all oxiranes could be converted. Conversely, modified DETA never crystallized. Assuming that the functionality of modified DETA was lower than pure DETA functionality (as explained in Section 7.3.6), all the amino groups that reacted with epoxy groups and epoxy groups in excess were detected by NIR. Epoxy groups could not react together by an etherification reaction which would need a higher temperature. DGEBA–

DETA systems vitrify at room temperature in less than an hour, contrary to DGEBA–IPDA systems, which vitrify at 60°C. When we cured the DGEBA–DETA systems (after 3 h at room temperature), they were already vitrified, preventing any etherification reaction.

7.3.6

Influence of the Stoichiometric Ratio

Finally, the variation of the glass transition temperature for both systems (DGEBA–IPDA or DGEBA–DETA) versus the stoichiometric ratio (a/e) is reported (e.g., see Fig. 7.6) for either pure or “modified” materials. Usually, as the functionalities of epoxy and amine monomer were well defined, mixing materials at the stoichiometric ratio of 1 led to the formation of the most crosslinked network having the highest glass transition temperature. From Fig. 7.6 it can be

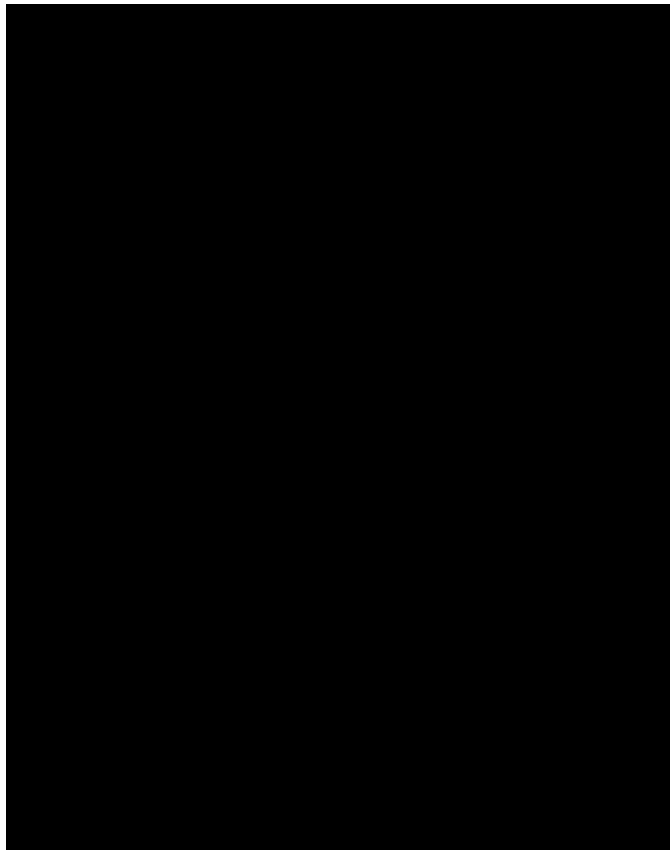


Fig. 7.6 Variation of glass transition temperature as a function of stoichiometric ratio.

seen that functionalities of 4 for IPDA, 5 for DETA, and 2 for the DGEBA epoxy monomers are correct (the maximum glass transition temperatures were observed for $a/e=1$, for both IPDA and DETA systems). But, for IPDA and DETA “modified” bulk materials, the maximum T_g values were observed for a stoichiometric ratio of 1.15. Indeed, after modification (i.e., formation of the organometallic complexes), the functionality of the organometallic complex was lower than the pure amine one. This assumption is in good agreement with findings on the μ -FTIR maps (see Section 7.3.5). Using those systems (DGEBA and IPDA or DETA on metallic substrates), the stoichiometric ratio had to be higher than 1 in order to obtain the highest crosslink density (i.e., the maximum glass transition temperature) and the best material properties [9]. Moreover for $a/e \leq 1.15$, the T_g values are always lower after modification than before (i.e., for pure materials). This decrease could be induced by a plasticization effect, due to small molecules such as unreacted organometallic complexes and/or water molecules diffusing within the liquid prepolymer following dissolution of the metallic hydroxide. In addition for $a/e \leq 1$, the epoxy groups are in excess. They might react together by an etherification reaction [10] to form a less reticulated network, with a lower T_g . Using DGEBA–IPDA systems and varying the stoichiometric ratio from 0.7 to 1.3, Bentadjine [3] has shown that etherification decreases when the stoichiometric ratio increases and that the etherification phenomenon increases for DGEBA–IPDA coatings 100 μm thick on titanium alloy. In all our systems the corresponding ether bands (1120 cm^{-1}) were also found.

7.4

Conclusion

When epoxy–amine prepolymers were applied on metallic substrates, interphases between the coating part, having the bulk properties, and the metallic surface were created. Amine chemisorption onto oxidic or hydroxidic metallic surfaces, concomitantly with partial dissolution of the surface oxide (and/or hydroxide) on the metal substrate, was observed, according to the basicity characteristics of the amine monomers ($\text{p}K_a \geq 10$). 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 organometallic complexes, or
- organometallic complexes formed on the metallic surface layer [6] diffused within the liquid monomer mixture (epoxy–amine).

Whatever the amines were, after application to metallic surfaces they were “modified” to form organometallic complexes having a lower functionality than the pure amines. These complexes might crystallize if their solubility limit was exceeded. During the curing cycle, uncrystallized organometallic complexes reacted with the epoxy monomer leading to a new network having a lower T_g , whatever the amine and the metal were. For IPDA systems, however, needle-like

structures were observed during all the curing cycles. They modify the polymer's mechanical properties by acting as short fibers. Even if crystals melted at 80 °C, they remained embedded into the vitrified polymer. Finally, thin coatings and bulk materials formed (for ISO 14679 mechanical tests) on metallic surfaces had the same interphase formed close to the metal.

Acknowledgments

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