Variation in Physical and Mechanical Properties with Coating Thickness in Epoxy–Diamine–Aluminum System

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ABSTRACT: The mechanical properties and glass-transition temperature within different thickness organic coatings made of diglycidyl ether of bisphenol A epoxy resin and 3-aminomethyl-3,5,5-trimethylcyclohexylamine hardener are determined. The coatings are deposited on aluminum alloy (1050) substrates after degreasing. Dynamic mechanical thermal analysis and differential scanning calorimetry experiments are carried out on debonded coatings before and after the material from the opposed surface to the polymer/metal interface is removed by polishing. The results clearly show that the values of the physical and mechanical properties in those coatings depend on their thickness, but there is no gradient of properties within such coatings. Therefore, at a given thickness, those properties are homogeneous within the coating. To gain a better fundamental understanding of this behavior, a qualitative model involving the chemical reactions that take place at the epoxy/metal interface and the related diffusion phenomena is given. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 891–895, 2005

Key words: coating; resin; glass transition; epoxy–aluminum interphase

INTRODUCTION

Epoxy resins and epoxy/aluminum alloy composites are widely used in many fields, such as the electronic and aerospace industries, because of epoxy's excellent thermal and chemical resistance and superior electrical and mechanical behavior. For example, epoxy resins have been used as anticorrosion protective coatings for metals and semiconductors in the electronics industry and as thermosetting adhesives in the aerospace industry. Thus, knowledge of the factors affecting the adhesion between epoxy polymers and aluminum surfaces is of substantial importance.

Among several curing agents employed to formulate epoxy resins, amines are undoubtedly the most extensively used. When epoxy–amine mixtures are applied onto metallic substrates and cured, a strong interaction between the amino groups and the metallic oxide and/or hydroxide takes place.[1]

Roche and coworkers[2–7] have widely studied the system of diglycidyl ether of bisphenol A (DGEBA)–3-aminomethyl-3,5,5-trimethylcyclohexylamine (IPDA)–aluminum and found that the chemical, physical, and mechanical properties of the coating materials differed from those of the bulk as a function of the coating thickness. They argued that this behavior corresponded to the formation of a thick interphase between the substrate and the bulk material. Thus, the polymer/substrate interphase should be a complex region containing gradients of chemical, physical, and mechanical properties. With this idea in mind, they developed a three-layer model (bulk coating/interphase/substrate) to evaluate the residual stress profile along the coating thickness. Thus, the calculated residual stress profile strongly depends on the Young's modulus values postulated for each position along the coating thickness. The practical adhesion of the coatings to the aluminum substrate, characterized as the ultimate load or the ultimate displacement in a three-point flexure test (ISO 14679-1997), was then found to correlate with the calculated residual stress at the interphase/metal interface. Indeed, when residual stresses at the interphase/metal interface increased, the ultimate load decreased.

Because we were interested in the chemical, physical, and mechanical properties of epoxy resin composites filled with aluminum powder and how the results reported by Roche et al.[2–7] could affect them, we focused our work on the determination of the mechan-

ical properties and the glass-transition temperature within the postulated interphase region. This was accomplished by measuring them in the debonded coating before and after the material from the opposed surface to the polymer/metal interface was removed by polishing.

EXPERIMENTAL

Materials

The metallic substrate used was a 1 mm thick commercial rolled 1050 aluminum alloy (Aluar Argentina). Aluminum sheets were cut into rectangles (60 × 60 mm²). Before any polymer application, the substrate surfaces were treated by ultrasonic degreasing in acetone for 15 min, drying off by flowing hot air and 15 min in an oven at 120°C, and cooling to room temperature.

Several layers of a rectangular (45 × 30 mm²) frame of Teflon (50 μm thick) were stuck together with the treated metallic sheet using double-faced adhesive tape in order to obtain the desired liquid coating thickness.

The epoxy prepolymer and curing agent were DGEBA LY 556 and IPDA HY 2962, both from Ciba Geigy. The epoxy resin was mixed with the hardener by stirring at room temperature under a vacuum for 30 min. A stoichiometric ratio (aminohydrogen/epoxy) of 1 was used.

The degased mixture was poured into a mold cavity placed on a metallic surface and spread with a cylindrical glass rod. For bulk materials, 45 × 30 × 15 mm³ prismatic pieces were prepared using a Teflon mold.

The curing cycle was 30 min at 30°C, 30 → 60°C at 1°C C/min, 2 h at 60°C, 60 → 140°C at 1°C/min, 1 h at 140°C, 140 → 190°C at 0.25°C/min, 6 h at 190°C, and cooling in the oven to 25°C.

Four coated sheets for each coating thickness and three bulk samples were prepared. After curing and cooling, coated 25 × 5 mm² samples were cut from the central part of the coated sheet with a diamond saw. Bulk material 25 × 5 × 0.6 mm³ samples were obtained with the same procedure applied on the central parts of the prismatic pieces. The measurement of the coating thickness (0.065–0.485 mm), after removal from the metallic substrate, was performed using a micrometer (sensitivity ±5 μm).

Methods

All mechanical and thermal characterizations were carried out on debonded coatings.

Differential scanning calorimetry (DSC) experiments were performed in a Shimadzu DSC 50 apparatus to determine the glass-transition temperature
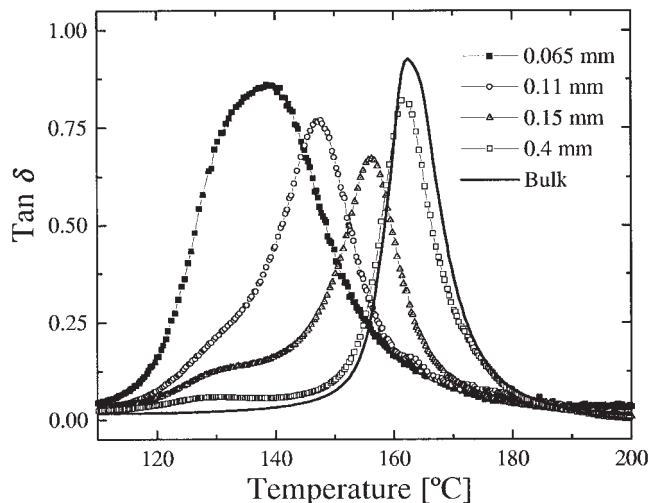

Figure 1 The loss tangent (tan δ) as a function of temperature for the bulk material and coatings with different thicknesses.

(T_g) of epoxy resins at a rate of 10°C/min from 30 to 200°C.

Dynamic mechanical thermal analysis (DMTA) experiments were carried out in a Rheometric Scientific DMTA IV apparatus. Measurements were performed in rectangular tension mode with an initial gauge length of 15 mm. The sample was deformed sinusoidally to a controlled strain amplitude of 6×10^{-4} at a fixed frequency of 1 Hz. The temperature was varied from 25 to 200°C using a heating rate of 2°C/min. This type of test allows us to obtain information about the dependence of the storage modulus (E'), loss modulus (E'') as well as the ratio $E''/E' = \tan \delta$ (loss tangent) as a function of temperature.

Two samples for each coating thickness were measured with both DSC and DMTA.

RESULTS AND DISCUSSION

Figure 1 shows the loss tangent as a function of temperature for the bulk material and coatings with different thicknesses. The T_g for each specimen is identified as the temperature at the maximum of the tan δ peaks. A significant shift of these peaks to lower temperatures is observed with decreasing thickness values.

The T_g values obtained from DMTA are plotted versus the coating thickness in Figure 2. The results from DSC measurements on the same coatings are also plotted. Both curves show the same tendency with the coating thickness (t_c). The T_g values from the DMTA measurements are higher than those from the DSC tests because of the well-known fact that an increase in the test frequency shifts the T_g to higher values.[8] For thinner coatings (0.065 < t_c < 0.25 mm) a gradient
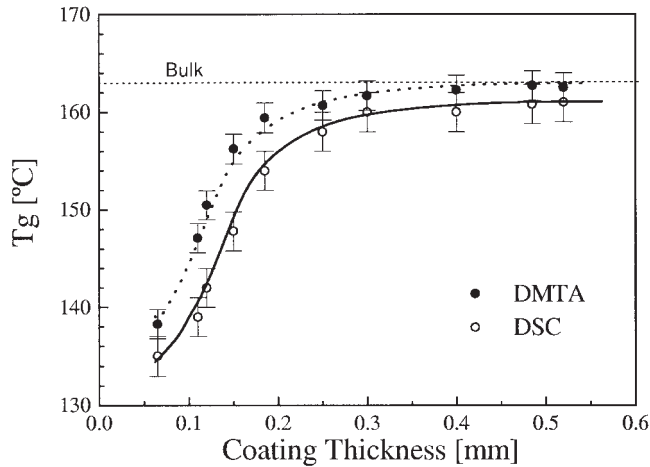
Figure 2 The glass-transition temperature (T_g) of the coating as a function of the coating thickness.

region for the T_g values is observed whereas for thick coatings ($t_c > 0.25$ mm) these values remain close to the bulk one. The values of their storage modulus that were obtained from DMTA data at 53°C are plotted versus the coating thickness in Figure 3. The storage modulus decreases as the coating thickness increases within the gradient region. The behavior of the glass-transition temperature and the storage modulus with the coating thickness agrees with those reported by Roche and coworkers in similar coating materials.[4–6] They propose that these experimental results define an interphase between the substrate and the bulk material.

Considering the hypothesis that a thick interphase is created between the substrate and the bulk material, one should expect to measure lower T_g values and higher E'values in the coating if the material from the
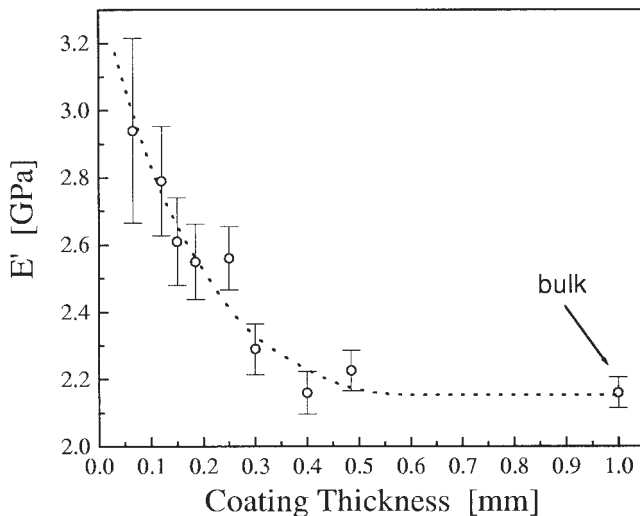

Figure 3 The storage modulus (E') of the coating, measured at 53°C, as a function of the coating thickness.
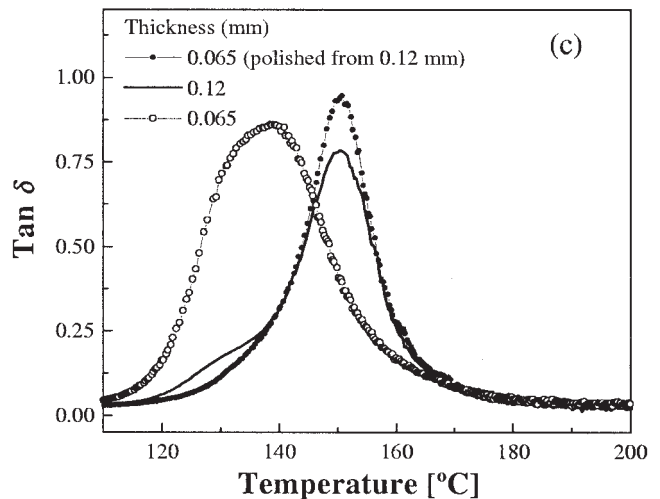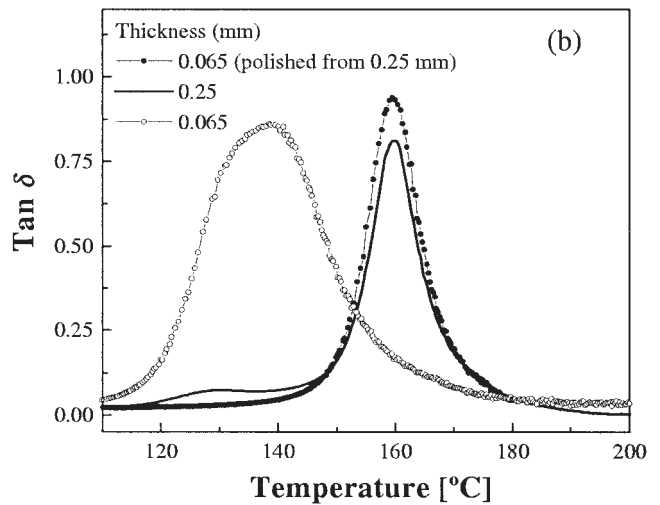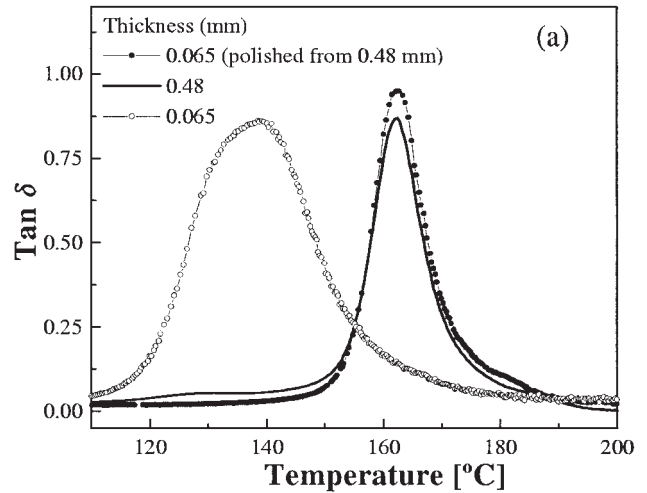

Figure 4 A comparison of the loss tangent (tan δ) curves for unpolished and polished coating specimens.

opposed surface to the polymer/metal interface is removed by polishing. Thus, we took three samples with initial coating thicknesses of 0.48, 0.25, and 0.12 mm. They were polished from the opposed surface to
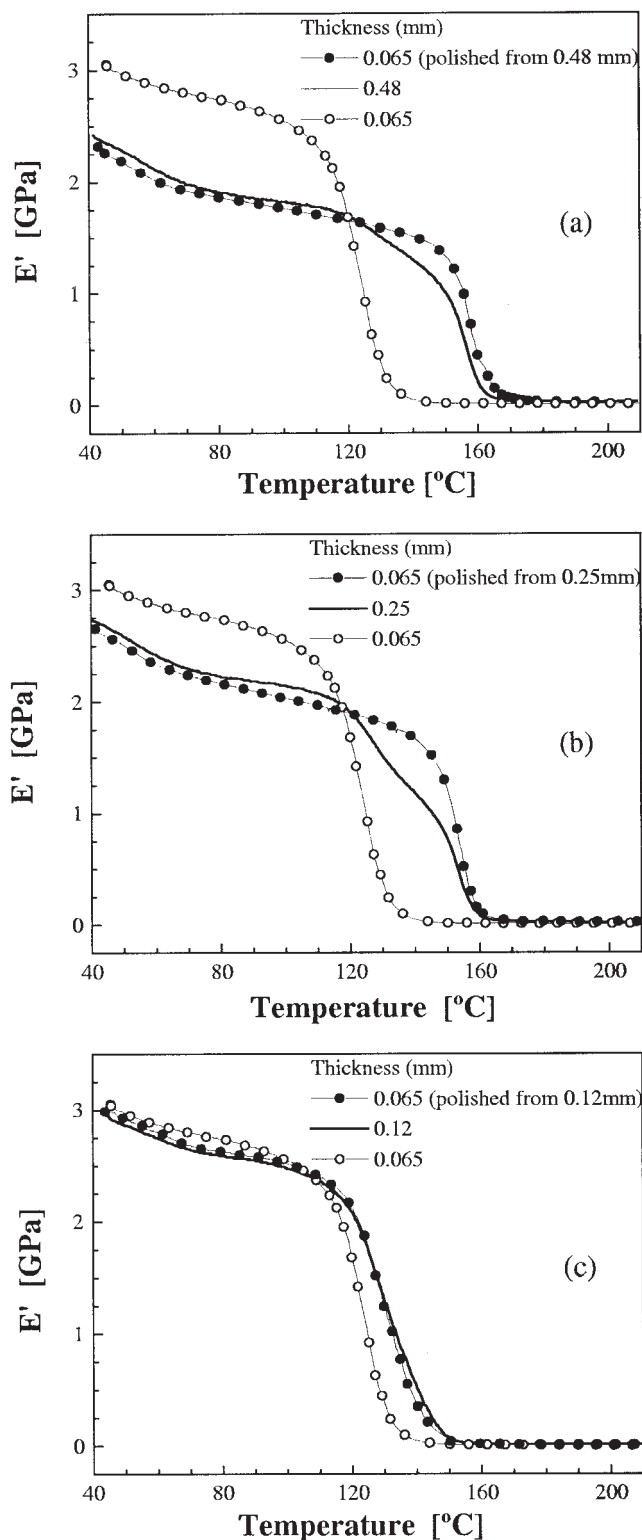
Figure 5 A comparison of the storage modulus (E') curves for unpolished and polished coating specimens.

the polymer/metal interface to a thickness of 0.065 mm and their loss tangent and storage modulus were measured as a function of temperature.

Figures 4(a) and 5(a) show a comparison between the results obtained for the sample with 0.48-mm orig-

inal coating thickness, the sample polished from a thickness of 0.48 mm to a thickness 0.065 mm, and a sample whose original thickness was 0.065 mm. Clearly, there is no increment of the value of E' nor a decrement in the value of T_g in the coating when the material from the opposed surface to the polymer/metal interface is removed by polishing. The same behavior is obtained with the samples of 0.25- and 0.12-mm initial coating thicknesses as shown in Figures 4(b) and 5(b) and 4(c) and 5(c), respectively. These results were confirmed by DSC measurements on similar samples. Therefore, both the storage modulus and the glass-transition temperature of these coatings depend on their thicknesses. However, for a given thickness, these properties are homogeneous within the coating.

The results obtained in our work show that the variation in physical and mechanical properties with the coating thickness in the epoxy–diamine–aluminum system does not define a thick interphase between the substrate and the bulk material.

The interesting work done by Roche and coworkers[4–7] describes the chemical reaction observed when epoxy–diamine is applied onto a metallic substrate, leading to a dissolution of the surface oxide and/or hydroxide followed by metallic ion diffusion. Metallic ions react by coordination with the amine groups of the diamine monomer to form organometallic complexes. When the complex concentration is higher than its solubility limit, complexes crystallize as sharp needles. During the curing cycle, uncrystallized organometallic complexes react with the epoxy monomer to form a new epoxy network with a lower T_g and the crystallized complexes act as short fibers in the organic matrix, leading to an increase of the elastic modulus. Thus, the proposed mechanism has at least three reaction times: the reaction time for surface oxide and/or hydroxide dissolution (τ_1), the diffusion time for the metallic ion into the liquid polymeric mixture (τ_2), and the reaction time for the organometallic complex formation (τ_3).

Roche et al.[2–7] proposed that their results on the variation in the physical, chemical, and mechanical properties with the coating thickness in the epoxy–diamine–aluminum system could be explained considering that τ_2 is longer than τ_1 and τ_3. In fact, in their work, the interphase formation is related to the spatial concentration of metallic ions and that is governed by a diffusion phenomenon. This spatial concentration of metallic ions could form a spatial concentration of organometallic complexes. As soon as the solubility product of organometallic complexes is formed, part of the organometallic complexes may crystallize, giving a spatial concentration of crystals; then, the Young's modulus within the coating would vary from the substrate surface. Of course, the remaining part of the organometallic complexes, which do not crystal-

lize, will have a spatial concentration and then the glass-transition temperature within the coating will also vary from the substrate surface. However, this picture contradicts our experimental results.

We understand that the variation observed in the physical, chemical, and mechanical properties with the coating thickness in the epoxy–diamine–aluminum system can be explained in a different way, assuming the following: the chemical reactions proposed by Roche and coworkers[2–7] are valid, the reaction time τ_2 is shorter than τ_1 and τ_3, and the amount of available superficial oxide and/or hydroxide to dissolve is fixed by the superficial treatment of the substrate. The first assumption allows us to talk about reaction products identical to those appearing in the mechanism proposed by Roche et al.[2–7] The second assumption enabled us to propose that, whatever the thickness of the coating can be, the concentration of metallic ions in the liquid monomer is homogeneous before the curing cycle. Then, the crystallized organometallic complexes and those not crystallized would be distributed homogeneously, giving a homogeneous storage modulus and glass-transition temperature within the coating, in agreement with our experimental results. The third assumption is the key to understanding why different physical, chemical, and mechanical properties are obtained when the coating thickness varies. Let us consider that the contact time between the liquid prepolymer and the metallic substrate is long enough to finish the reaction, from one or the other side, between the IPDA monomer and the superficial oxide and/or hydroxide. Because the stoichiometric ratio of the prepolymer mixture is fixed, the amount of available IPDA monomers for the contact area linearly increases with the thickness. Then, for much thinner coatings the reaction finish from the IPDA side and the concentration of organometallic complexes is high but remains constant when the thickness increases. However, for a given thickness, the reaction starts to finish from the oxide and/or hydroxide side and the concentration of organometallic complexes begins to decrease when the thickness increases. Now, the concentrations of the crystallized organometallic complexes and those not crystallized will follow the same evolution with the thickness of the coating because they depend on the difference between the total concentration and the solubility limit. That means the Young's modulus and the glass-transition temperature will remain constant for very thin coatings, but the Young's modulus will decrease and the glass-transition temperature will increase as the thickness increases for thicker ones. This picture is in agreement with our experimental findings and those of Roche and coworkers.[2–7]

Finally, our results indicate that the residual stress at the polymer/metal interface of DGEBA–IPDA layers deposited onto 1050 aluminum should be calculated using a bilayer model with a uniform elastic modulus for the polymer layer. The value of the elastic modulus depends on the thickness and the curing cycle of the polymer layer.

CONCLUSIONS

It is well known that, when prepolymer DGEBA–IPDA is applied on an aluminum substrate and cured, the obtained organic layer has chemical, physical, and mechanical properties that are dependent on its thickness. This behavior was taken as an evidence of the formation of a thick interphase between the substrate and the bulk material. However, in this work we demonstrated experimentally that there is no gradient of physical and mechanical properties within such coatings. Thus, the residual stress generated at the polymer/metal interface of such systems should be calculated using a bilayer model with a uniform Young's modulus for the polymer layer instead of a three-layer model with an interphase region where the Young's modulus varies from the substrate surface.

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