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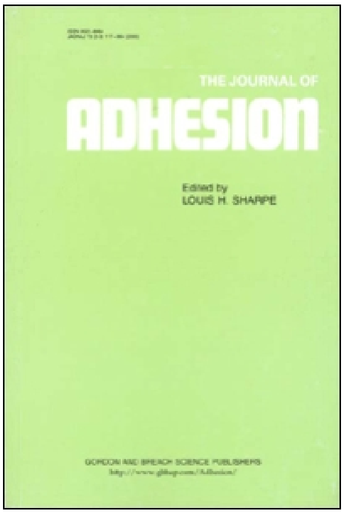

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Adhesion Mechanisms at Amine-Cured Epoxy/Aluminium Interfaces*

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Because the structure and the chemical composition of the interface can have a large effect on the adhesion properties of polymeric materials to metallic surfaces, many investigations have concentrated on the study of the interphase region. However, the complexity of the materials often leads to the use of model compounds to mimic the interfacial reaction. We have presented a critical discussion of three different approaches which have been used to understand the adhesion mechanism at amine-cured epoxy/aluminium interfaces: i) fracture of "real world" joints; ii) deposition of model (amino-alcohol) molecules on "real world" substrates; i) deposition of model (amino-alcohol) molecules on clean, oxidised and hydroxylated Al (100) surfaces. We have shown that model compounds can adequately duplicate the interface chemistry observed in "real world" joints. However, a detailed understanding of the exact nature of the interactions and of the role of the different reactive sites can only be achieved through studies performed on a model surface under controlled ultrahigh vacuum conditions.

KEY WORDS: adhesion mechanisms; adsorption of resin mimics on aluminium; epoxy-aluminium interfaces; amine-cured epoxy mimics; X-ray photoelectron spectroscopy; infrared spectroscopy; high resolution electron energy loss spectroscopy (HREELS)

INTRODUCTION

Even though epoxide adhesives are extensively used in the aerospace and automotive industries, the exact nature of the bonding of epoxy resins on metals is still not fully understood. The surface science approach looks promising for characterising the interface at a molecular level. In principle, all the surface analysis techniques can routinely achieve a suitable resolution, but most of them are limited by their inability to probe buried interfaces. To face this limitation, the polymer/solid interface must be prepared either by fracture of the adhesive joint or by deposition of submonolayer to few-monolayer quantities of the polymer on the metallic surface. However, even when using such a procedure, the chemical complexity of the epoxy resin often leads to great difficulty in the interpretation of the adhesion mechanism. Thus, model compounds are often used to simulate the polymer system.

In this paper, a critical discussion of three approaches which have been used to understand the detailed adhesion mechanism of amine-cured epoxy resins on aluminium

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substrates will be presented: i) fracture of "real world" joints; ii) deposition of a model compound (amino alcohol) on the "real world" metallic surface; iii) deposition of a model compound (amino alcohol) on a model metallic surface. Examples will be taken either from the literature or from the work of the author's group to illustrate the nature of the information which can be deduced from the respective approaches.

"REAL WORLD" INTERFACES

A combined X-ray Photoelectron Spectroscopy (XPS) and Infrared Reflection-Absorption Spectroscopy (IRAS) study has been performed by Dillingham and Boerio[1] on epoxy/aluminium adhesive joints. Joints were prepared by applying a DGEBA resin (Epon 828™, Shell Chemical Co.) cured with triethylenetetraamine (TETA, Fisher Scientific Co.) on mechanically-polished beams of 2024-T3 aluminium substrates. Specimens were constructed with a geometry that allowed fracture to be initiated close to the interface. Figure 1 shows the Cls peaks obtained in XPS from bulk-cured adhesive (Fig. 1A) and from the epoxy side of the fracture surface (Fig. 1B). The curve-fitting process that was used allowed an unequivocal establishment of three peaks representing C—C and C—H bonds (at 284.6 eV), C—N bonds (at 285.6 eV) and C—O bonds (at 286.3 eV). Figure 1 shows that, on the adhesive fracture surface, there is an increase in the peak area corresponding to C—N bonds and a decrease in the peak area corresponding to C—O bonds, when compared with the bulk-cured adhesive. This was ascribed to an enhancement of the curing mechanism near the oxide surface. During the curing reaction between TETA and DGEBA, the primary amines of the curing agent open up the glycidyl ether ring of the resin through nucleophilic attack, thus resulting in the formation of a C—N bond at the expense of a C—O bond. Additional information was obtained from the N1s spectra of both the bulk resin and the fracture surfaces, as shown in Figure 2. Applying the fitting process leads to the establishment of two components in the N1s peak, respectively corresponding to nitrogen atoms that are bonded to carbon and hydrogen atoms (at 398.0 eV) and to amine nitrogens that are protonated (at 399.5 eV). From Figure 2, it can be seen that the high-energy component is very small in the bulk cured resin (Fig. 2A) while it represents about one-half of the whole nitrogen peak on the aluminium side of the fracture surface (Fig. 2C). This increase in the high-binding-energy nitrogen species was ascribed to the protonation of amines of the curing agent by the hydroxyl groups which are present on the surface of the mechanically-polished 2024-T3 aluminium substrates. The presence of such a large percentage of protonated amino nitrogens near the adherend surface suggests that hydroxyls are abundant in this region. Because both the initiation and the propagation steps of the polymerization of epoxy resins require the presence of a proton donor,[2] the high concentration of hydroxyls near the aluminium oxide surface can, thus, explain the observed enhancement of the curing mechanism near the interface.

MODEL COMPOUND/"REAL WORLD" ADHEREND INTERFACES

Because of the chemical complexity of the epoxy resins, model molecules or resin mimics have often been used to study the interfacial interactions. In this respect, amino

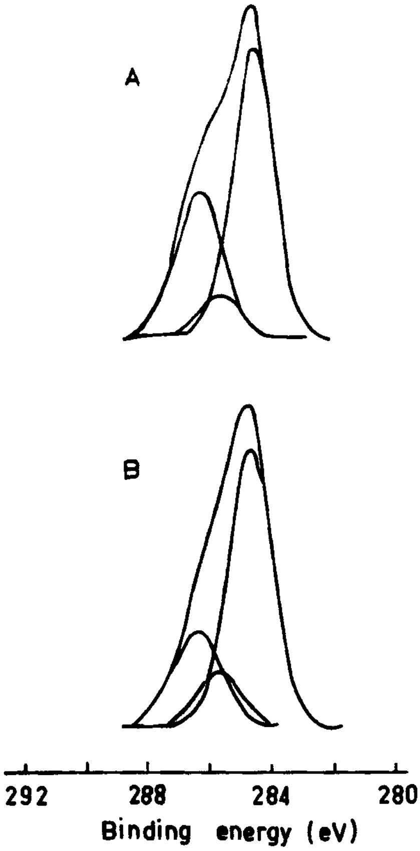

FIGURE 1 C 1s XPS data obtained for: A) bulk cured adhesive; B) adhesive fracture surface. After Dillingham and Boerio, Ref. 1.

alcohols have been used in several studies to simulate amine-cured epoxy resins. In particular, *1*-amino-*2*-hydroxyethane (monoethanolamine), which is the most simple molecule containing an amino functionality β to an alcohol group, has been adsorbed onto plasma-grown aluminium.[3] Although this molecule is not a resin mimic, the interaction of *1*-amino-*3*-hydroxypropane with plasma-grown aluminium oxides has also been examined.[4, 5] Because curing is often not fully achieved in many industrial processes, molecules containing a secondary amino functionality, such as diethanolamine[6] or *N*-propyl-*2*-hydroxybutylamine[7, 8] have also been used to mimic partially-cured resins on various aluminium oxide surfaces (air-oxidised,[6] plasma-grown[7] or phosphoric acid anodised).[6, 8] Finally, the adduct of reaction of the diglycedylether of bisphenol A with excess diethylamine, which contains tertiary nitrogens, has been adsorbed onto plasma-grown aluminium oxide[9] or anodised aluminium[10] to simulate a fully-cured resin. Inelastic Electron Tunnel Spectroscopy (IETS),[3-5, 7, 9] X-ray Photoelectron Spectroscopy (XPS)[6, 8, 10] or Static Secondary Ion Mass Spectroscopy (SSIMS)[8] were used to monitor the adsorption process.

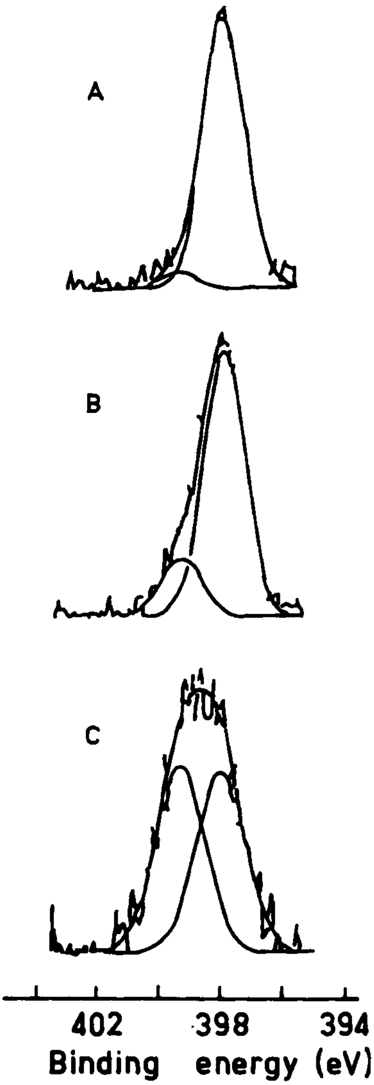

FIGURE 2 N 1s XPS data obtained for: A) bulk cured adhesive; B) adhesive fracture surface and C) adherend fracture surface. After Dillingham and Boerio, Ref. 1.

The intensity reduction of the υ_{O-H} band characteristic of surface hydroxyl groups, observed in all the vibrational studies, has generally been ascribed to the elimination of these species by reaction with the alcoholic hydroxyl hydrogen of the molecule, leading to the formation of alkoxide species. However, the SSIMS data obtained by Affrossman and MacDonald[8] during adsorption of *N*-propyl-2-hydroxybutylamine on phosphoric acid anodised aluminium seem to indicate that the alcohol group is retained in the adsorbed species, thus rather suggesting a polar interaction of the alcohol group of the molecule with the surface.[8] However, caution must be exercised when comparing results obtained on a very thin pure oxide layer and on a thick layer covered with a phosphate monolayer. The difference in surface chemistry can induce a different binding mechanism.

If, with the exception of this last study, the formation of an alkoxide moiety is generally accepted, the interaction of the amino functionality with the surface is still the subject of much controversy. In fact, even though the interpretations are largely divergent, the experimental data look very similar in all the experiments described above: NH_2 stretching modes are observed in the 3100–3300 cm^{-1} region and/or a Nls XPS peak appears at a high binding energy. The NH_2 stretching modes are ascribed to either free unperturbed amino groups (Fig. 3a),[3, 5] to NH_2 groups coordinated to a (Lewis acid site) aluminium ion (Fig. 3b)[4, 9, 10] or to an amine protonation effect on the Brönsted acid sites of the surface (Fig. 3c).[7] In an infrared study of a 10^{-2} mol l^{-1} solution of monoethanolamine in CCl_4, Fauquet has shown that, for *1*-amino-*2*-hydroxyethane, the infrared bands characteristic of free amino groups should appear in the 3400–3500 cm^{-1} region.[11] Thus, we think that the NH_2 stretching frequency observed in all the studies presented here is too low to correspond to free NH_2 groups. However, it looks difficult to discriminate between coordination of the N atom to an aluminium ion or amine protonation. Additional information can be obtained using XPS, considering that a quaternary ion should present a N ls binding energy around 401.5 eV (with reference to the C 1s signal at 285.0 eV).[12] In fact, amine protonation is often deduced[6, 8] from the appearance of a peak on the high-binding-energy side of an initial N 1s peak which is due to either contamination or amine groups removed from surface. However, because bonding via N lone-pairs coordinated to acidic metallic ion sites would also imply electron donation from the nitrogen, a shift of the N 1s peak binding energy towards high values is also expected in that case and such a mechanism has also been proposed.[10] It must be noted that a comparison of absolute binding energies of the N 1s peak between different authors is meaningless, because of the general lack of information concerning the spectrometer calibration and the eventual existence of several nitrogen species. In fact, due to the complexity of the surface chemical state, both Lewis and Brönsted acid sites are likely to be present on "real world" surfaces, leading to the coexistence of both types of binding mechanisms, as suggested in a study of *1*-amino-*2*-hydroxyethane adsorption onto alkaline-cleaned steel sheets.[13]

MODEL COMPOUND/MODEL SURFACE

Adsorption of model compounds on "real world" surfaces has shown that alkoxide species were formed following interaction of the alcohol termination of the molecule with the surface hydroxyls. However, it is not clear whether surface hydroxyls are the only surface species which can react. In fact, Affrossman and MacDonald proposed a hydrogen bonding between the alcoholic hydroxyl *hydrogen* and both hydroxyl and oxide sites at the surface in the case of *N*-propyl-*2*-hydroxybutylamine adsorption on phosphoric acid anodised aluminium.[8] Careful control of the chemical state of the metallic surface is necessary to understand fully the detailed mechanism of interaction.

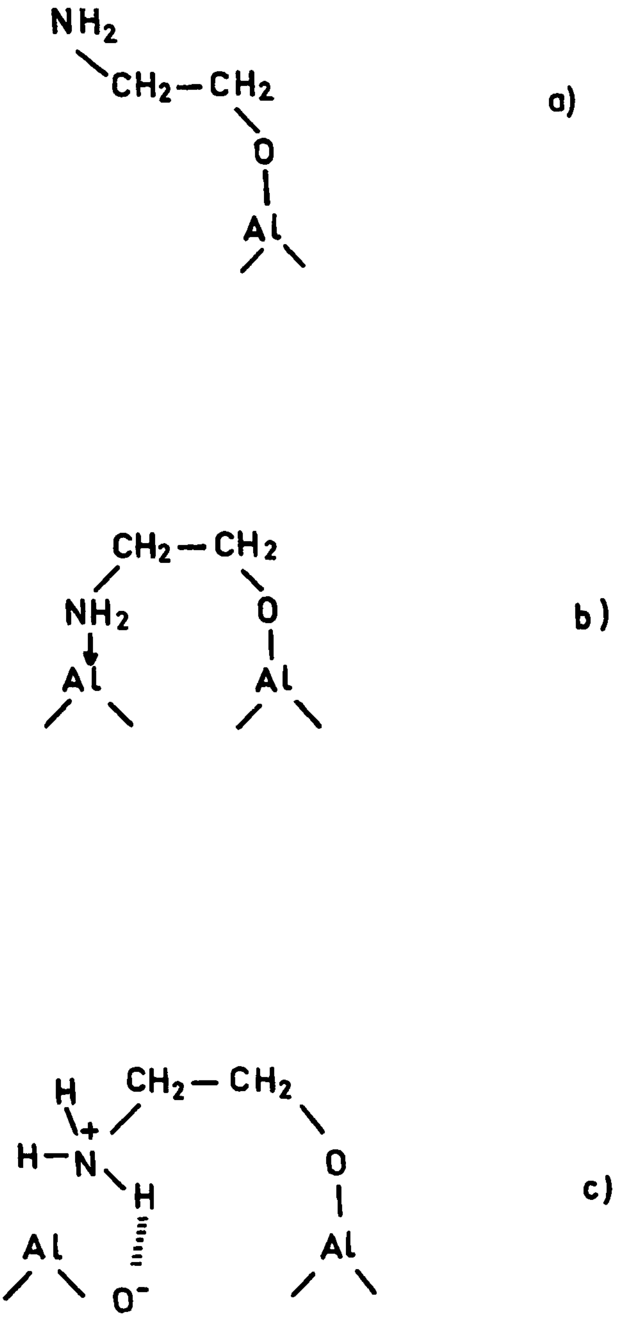

FIGURE 3 Possible modes of interaction of the amino functionality with aluminium "real world" surfaces: a) free amino groups; b) NH_2 groups coordinated to an aluminium ion; c) amine protonation effect.

To fulfill this last requirement, we have investigated the interaction of *1*-amino-2-hydroxyethane with an aluminium (100) single crystal surface which has been cleaned, then oxidised or hydroxylated under ultrahigh vacuum conditions. Combined Auger Electron Spectroscopy (AES) and High Resolution Electron Energy Loss Spectroscopy (HREELS) experiments have shown that the detailed mechanism of the interaction was strongly dependent on the surface chemical state of the substrate.[14] Bonding with clean (oxide free) Al (100) occurs via nitrogen lone-pairs coordinated to soft acidic aluminium atoms (Lewis-like acid-base reaction). Bonding with oxidised Al (100) is via *oxygen* lone-pairs of the alcohol termination of the molecule coordinated to hard acidic aluminium ions (Lewis-like reaction). Interaction with hydroxylated Al (100) also occurs through the molecule's alcohol termination but, this time, leads to formation of an alkoxy species and elimination of water. Because OH species are always present on "real world" surfaces, formation of the alkoxy species should be favoured. However, it seems possible to observe electron donation from the *oxygen* of the alcohol group towards the aluminium ion, if the concentration of OH species is low enough.

Although no long-range order could be observed on our very thin oxide (hydroxide) films, we have suggested that they could locally present a γ-like alumina spinel

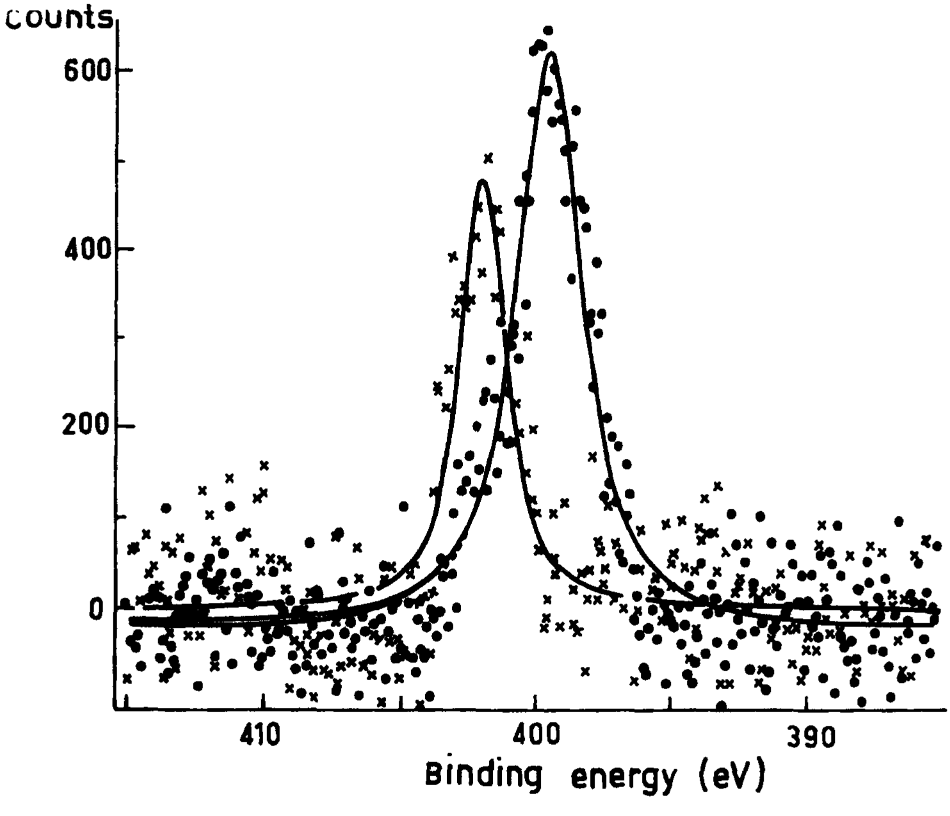

FIGURE 4 N 1s XPS data observed following adsorption of monoethanolamine on: a) clean Al (100) (dots); b) hydroxylated Al (100) (crosses).

structure.[14] Hence, the difference in frequencies observed for the Al-O stretching mode in the HREEL spectra obtained following monoethanolamine adsorption on oxidised aluminium (640 cm^{-1}) or on hydroxylated aluminium (870 cm^{-1}) has been interpreted in terms of different adsorption geometry. Interaction of monoethanolamine with oxidised Al(100) occurs with fixation of the oxygen atoms of the molecule on top aluminium sites, whereas oxygen atoms of the molecule are located in tetrahedral sites below the hydroxylated surface.

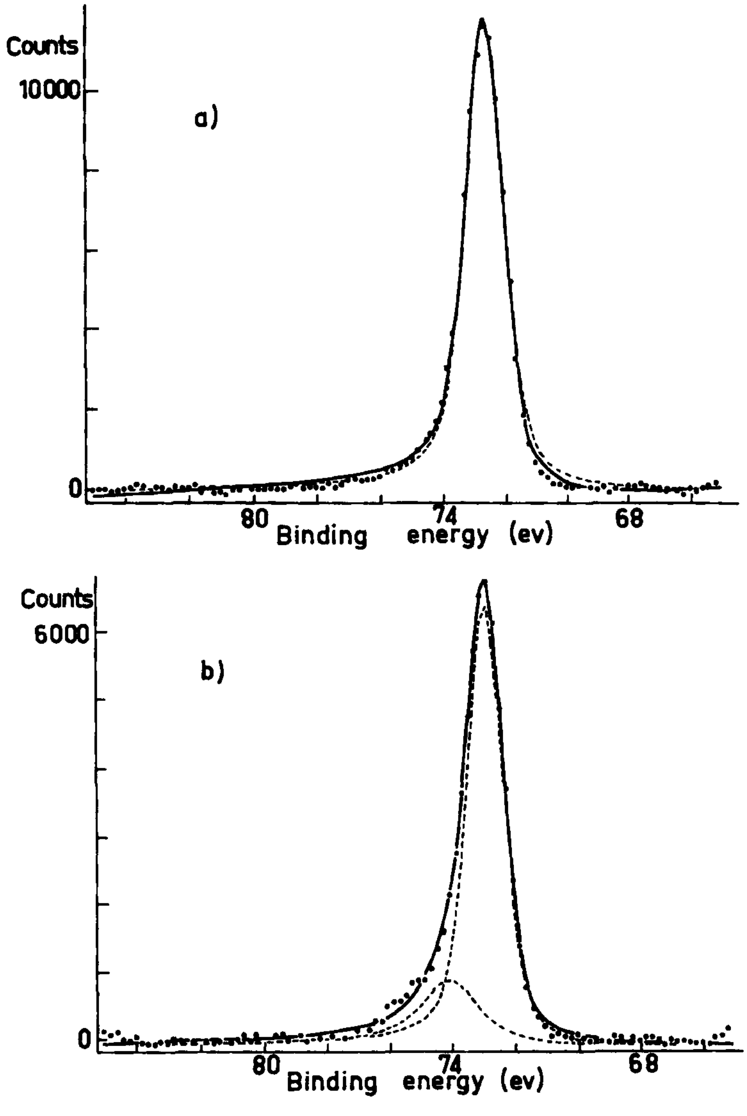

FIGURE 5 Al 2p XPS data observed for: a) clean Al(100); b) following monoethanolamine adsorption on clean Al(100).

XPS experiments have also been carried out on the same model system.[15] However, it has not been possible to follow adsorption on oxidised Al(100) in the XPS chamber. Due to a high residual water pressure, OH species were always present at the surface. Following adsorption of monoethanolamine on clean Al(100), Figure 4a shows that a N 1s peak is emerging at 399.5 eV (by reference to the clean Al 2p signal at 72.6 eV). Simultaneously, a shoulder is appearing at 73.9 eV, on the high-binding-energy side of the Al 2p peak (see Fig. 5), which can be ascribed to Al-N bonds. The low binding

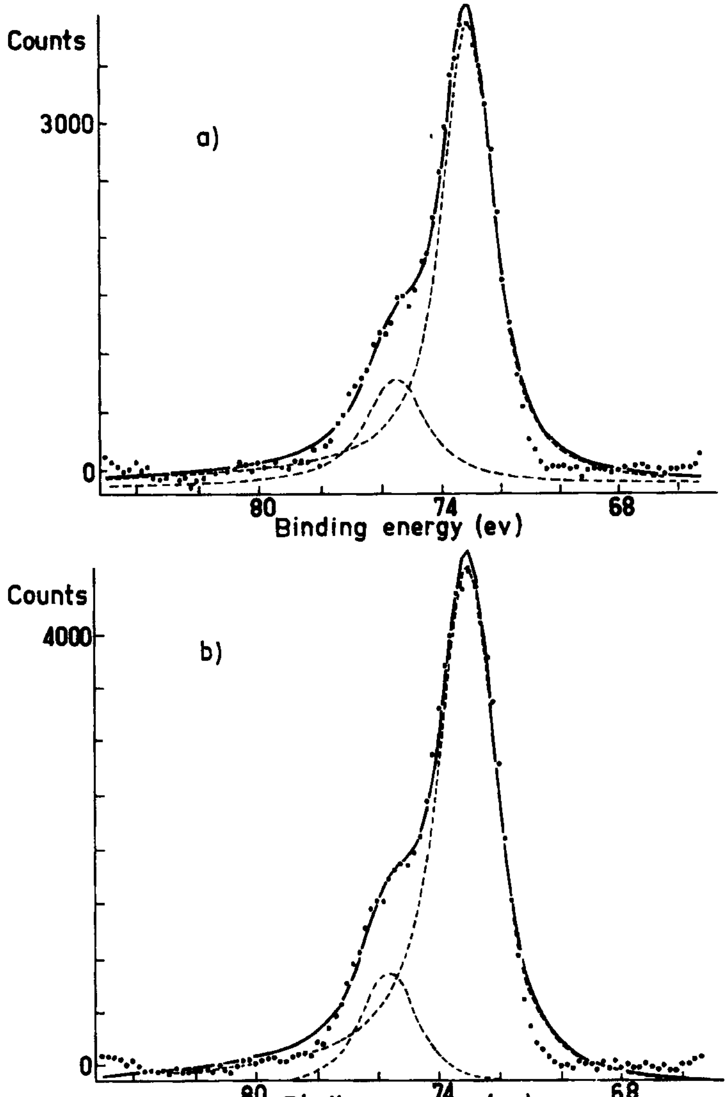

FIGURE 6 Al 2p XPS data observed for: a) hydroxylated Al(100); b) following monoethanolamine adsorption on hydroxylated Al(100).

energy value of the N 1s peaks thus corresponds to a small charge transfer due to the formation of a weak bond between Al and N, as expected following reaction of the (hard Lewis base) amino functionality with the (soft Lewis acid) metal. Following adsorption on hydroxylated Al (100), the N 1s peak appears at 401.8 eV (see Fig. 4b), thus indicating a large charge transfer. Again, it seems difficult to discriminate between amine protonation and coordination of the nitrogen atom to an aluminium ion. The absence, in the decomposition of the Al 2p peak, of the Al-N component at 73.9 eV (Fig. 6) seems to favor the amine protonation mechanism. However, the presence of a small Al-N peak might be disregarded during the decomposition procedure, and the possibility of nitrogen coordination to an aluminium ion cannot be completely set aside from this experiment only. Work is under progress on oxidised Al(100) and a clearer conclusion could be drawn if nitrogen coordination to aluminium can be observed on such a surface, where protonation is impossible.

CONCLUSION

In this paper, we have critically presented three different approaches to understanding the chemical interactions involved at amine-cured epoxy resins/aluminium interfaces: i) study of fractured "real world" joints; ii) deposition of model compounds on "real world" aluminium substrates; iii) deposition of a model compound on a ultrahigh vacuum cleaned, oxidised or hydroxylated aluminium (100) surface. The general agreement between experiments carried out using model compounds adsorbed on "real world" surfaces and results on fractured adhesive joints indicates that model compounds can adequately duplicate the interface chemistry of "real world" joints. Moreover, a detailed understanding of the exact nature of interactions, and of the role of the different reactive sites involved in the adhesion mechanism, requires careful control of the surface geometry and chemical state of the substrate which can only be achieved through studies performed on a model surface under controlled ultrahigh vacuum conditions. However, it must be kept in mind that such surfaces are rather artificial, not being submitted to the usual surface treatments; consequently, there are modes of adsorption on "real world" surfaces which cannot be mimicked by model studies.

References

1. R. G. Dillingham and F. J. Boerio, *J. Adhesion* **24**, 315 (1987).
2. B. A. Rozenburg, in *Advances in Polymer Science*, Vol. 75, K. Dusek, Ed. (Springer-Verlag, Berlin, 1986).
3. R. J. Turner, N. M. D. Brown and D. G. Walmsley, *Vacuum* **31**, 603 (1981).
4. S. D. Williams and K. W. Hipps, *J. Catalysis* **78**, 96 (1982).
5. N. M. D. Brown, R. J. Turner and D. G. Walmsley, *J. Molecular Structure* **79**, 163 (1982).
6. J. A. Kelber and R. K. Brow, *Appl. Surf. Sci.* **59**, 273 (1992).
7. N. M. D. Brown, R. J. Turner, S. Affrossman, I. R. Dunkin, R. A. Pethrick and C. J. Shields, *Spectrochimica Data* **40B**, 847 (1985).
8. S. Affrossman and S. M. MacDonald, *Langmuir* **10**, 2257 (1994).
9. S. Affrossman, N. M. D. Brown, R. A. Pethrick, V. K. Sharma and R. J. Turner, *Appl. Surf. Sci.* **16**, 469 (1983).
10. H. Bolouri, R. A. Pethrick and S. Affrossman, *Appl. Surf. Sci.* **17**, 231 (1983).
11. C. Fauquet, Thèse Université Pierre et Marie Curie, Paris (1992).

12. G. Beamson and D. Briggs, *High Resolution XPS of Organic Polymers; The Scienta ESCA 300 Database* (John Wiley and Sons, New York, (1992).
13. K. Dardenne, P. Dubot, L. Minel and M-G. Barthés-Labrousse, in preparation.
14. C. Fauquet, P. Dubot, L. Minel. M-G. Barthes-Labrousse, M. Rei Vilar and M. Villatte, *Appl. Surf. Sci.*, **81**, 435 (1994).
15. F. Demulder, L. Minel and M-G. Barthés-Labrousse, in preparation.