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The adsorption of an epoxy acrylate resin on aluminium alloy conversion coatings

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ABSTRACT

A thermodynamic study of the adsorption of an epoxy acrylate resin used for UV-cured coatings on two different anticorrosion pretreatments on aluminium alloys relevant to aerospace industry has been undertaken. Aluminium alloy Al2219 specimens, treated with an inorganic chromate based conversion coating (Alodine 1200S) and an organic titanium based conversion coating (Nabutan STI/310), were immersed in solutions of different concentrations of the resin and adsorption isotherms were determined by assessing the uptake of the adsorbate, as a function of solution concentration, by time-of-flight secondary ion mass spectrometry (ToF-SIMS). The results show different behaviour for the two substrates, which can be attributed to the organic component of the titanium based coating. In the case of the inorganic conversion coating a clear plateau is achieved at relatively low concentrations and at a lower level of adsorption than for the hybrid coating. The data for both the coatings conform well to the Langmuir model, the organic coating, as well as showing a higher level of adsorption of the resin, also presents oscillatory behaviour at low concentration, which is shown to be complementary to the behaviour of the reactive diluent included with the epoxy acrylate to aid processing. A discussion of this competitive adsorption of the epoxy resin and the diluent on the different substrates is presented, based on considerations of the chemistry of the systems under investigation.

1. Introduction

High strength aluminium alloys, because of their excellent properties, are traditionally used in aircraft applications. An alloy that satisfies many of the requirements of aircraft industry with good results is the 2xxx series, rich in copper, used for structural components [1]. Generally these alloys have a good corrosion resistance for most environmental exposures, however specific environmental conditions, such as long period storage in humid and/or salty environments, may trigger corrosion and therefore an additional protection is required. Numerous conversion coatings have been developed with the main purpose being not only the protection of aluminium from corrosion, but also the improvement of the adhesion of further treatments, such as paints and adhesives. The most widely used pretreatment in the aerospace industry is Alodine 1200S, manufactured by Henkel, because of its excellent performance as an anticorrosion layer and as a primer for further treatments. The presence of chromium VI in its formulation makes it potentially harmful to humans and environmentally undesirable, thus recent EU restrictions on the use of chromium VI have established the legislative requirement to replace Alodine 1200 with a chromium-free conversion coating [2]. A possible candidate to replace Alodine is the hybrid chemical conversion coating Nabutan STI/310, by NABU Oberflächentechnick GmbH, thus its general performance as an aluminium pretreatment needs to be investigated. An important aspect to be assessed is its capability of acting as a substrate for the application of paints, and this can be achieved with an investigation of the adsorption of polymers used in such coatings on the surface.

One of the main characteristics of polymers is that they can readily adsorb onto high surface energy solid surfaces. This property is the basis of the successful use of organic coatings and adhesives. They are usually applied as low viscosity liquids to inorganic substrates and they produce chemical and/or configurational interactions in the interphase region between substrate and coating. The understanding of these interactions is useful as a means of improving the performance of the coatings.

The adsorption from the gas phase is well known, but when the polymer is in the form of a liquid solution the process is not so simple, since a competition between the polymer and the solvent molecules for the active sites on the substrate may take place.

A well established method of obtaining information concerning polymer adsorption is the construction of adsorption isotherms,

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plots of the uptake of a compound at constant temperature versus its partial pressure (in gas phases) or concentration (in liquid solutions).

In gas phase adsorption the amount adsorbed is expressed as fractional coverage θ:

$$\theta=\frac{[\text{number of adsorption sites occupied}]}{[\text{number of sites available}]}$$

which can be expressed in terms of volume of gas adsorbed on the solid surface, V, and volume of the gas adsorbed when a monolayer coverage is reached, V_∞, at a specific pressure:

$$\theta=\frac{V}{V_\infty}$$

According to the energies of the bonds involved, the adsorption phenomenon can be distinguished by physisorption (weak van der Waals bonds) or chemisorption (donor–acceptor bonds, such as hydrogen bonds) with the physisorption process being less exothermic than chemisorption. An important difference between the two kinds of interaction is the effect that heat has on them: it reduces physisorption, breaking the weak bonds, which form as a result of adsorbate and substrate proximity, while it increases chemisorption, which has a significant activation energy.

An important model that describes well the majority of adsorption behaviour is the Langmuir model. Such a model is based on the following assumptions:

(1) a site can be empty or occupied;
(2) the adsorption process will terminate with monolayer coverage;
(3) all sites are equivalent;
(4) there are no lateral interactions between adsorbed species; and
(5) adsorption is reversible.

The last assumption implies that the process will reach a dynamic equilibrium, when the rate of adsorption equals the rate of desorption. This rate is proportional with the equilibrium pressure of the gas, or in the case of a liquid the solution concentration.

In mathematical terms:

$$\text{Adsorption}: m+v\rightarrow o.s. r_{ads}=k_1[m][v]$$

$$\text{Desorption}: o.s.\rightarrow m+v r_{des}=k_2[o.s.]$$

where m is the number of molecules, v is the number of vacant sites and $o.s.$ is the number of occupied sites, r_{ads} and r_{des} are the rates of adsorption and desorption, respectively, and k_1 and k_2 are the kinetic constants.

At equilibrium then:

$$r_{ads}=r_{des}=k_1[m][v]=k_2[o.s.]\rightarrow\frac{[v]}{[o.s.]}=\frac{k2}{k_1[m]}=\frac{1}{K[m]}$$

$$\text{with}\quad K=\frac{k_1}{k_2}$$

The total number of sites are $t.s.=v+o.s$, the fractional coverage θ is then:

$$\theta=\frac{[o.s.]}{[t.s]}=\frac{[o.s.]}{[o.s.]+[v]}=\frac{1}{1+\frac{[v]}{[o.s.]}}=\frac{1}{1+\frac{1}{K[m]}}=\frac{K[m]}{K[m]+1}$$

Applying the ideal gas law

$$PV=nRT\rightarrow\frac{n}{V}=\frac{P}{RT}\rightarrow C=\frac{P}{RT}$$

θ will be

$$\theta=\frac{[o.s.]}{[t.s.]}=\frac{KP}{KP+1}=\frac{V}{V_\infty}$$

Replacing V with a more general term Γ

$$\theta=\frac{\Gamma}{\Gamma_\infty}=\frac{KP}{1+KP}\rightarrow\frac{P}{\Gamma}=\frac{1}{K\Gamma_\infty}+\frac{P}{\Gamma_\infty}$$

and applying the Arrhenius equation

$$k_1=k_{10}\exp\left(\frac{-E_{ads}}{RT}\right),\quad k_2=k_{20}\exp\left(\frac{-E_{des}}{RT}\right)$$

$$K=\frac{k_1}{k_2}=\frac{k_{10}}{k_{20}}\exp\left(\frac{-(Eads-Edes)}{RT}\right)\rightarrow K=K_0\exp\left(\frac{Q}{RT}\right)$$

where k_{10} and k_{20} are frequency factors, E_{ads} and E_{des} are the energies of adsorption and desorption, respectively, and Q is the interaction energy.

When the equilibrium is reached and P is constant the extent of adsorption is given by the value of K, which will increase with a reduction of the system temperature and with an increase of interaction energy (stronger bonds between molecules and sites).

In the case of adsorption from a liquid solution the Langmuir equation becomes

$$\frac{c}{x}=\frac{1}{K\Gamma_\infty}+\frac{c}{\Gamma_\infty}\tag{1}$$

Plotting the quantity of solute adsorbed, x, against its concentration in solution, c, the outcome will be a curve that describes the capacity of the surface for the adsorbate and thus describes the thermodynamics of the adsorption process. By plotting c/x against c a straight line would result, with gradient $1/\Gamma_\infty$ and intercept $1/K\Gamma_\infty$ and Γ_∞ being monolayer coverage.

Direct analysis of the liquid phase can only lead to relative results since there is a competition between the solute and the solvent for the active sites. It is also important to choose an apolar solvent in such experiments to obviate the problems of substrate/solvent and solute(s)/solvent interaction [3]. This is overcome in the current work by the choice of toluene as suitable solvent, which is regarded as neutral from a Lewis acid/base perspective. In this manner interactions between solutes and substrate will not be impeded by solvent issues.

An important limit of the Langmuir model is the assumption that the adsorption enthalpy is not dependent on the coverage. Surfaces are often inhomogeneous, and even if they are not, as in the case of single crystal surfaces, as the coverage increases lateral interactions between adsorbed molecules and unoccupied sites may affect the heat of adsorption. Two other models take into account this important variation: Temkin and Freundlich. The Temkin isotherm assumes a linear relationship between P and the enthalpy of adsorption, ΔH_{ads}:

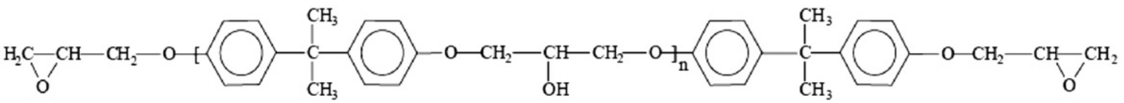
$$\theta=c_1\ln(c_2P)\tag{2}$$

where c_1 and c_2 are constants. The Freundlich model assumes that the heat of adsorption logarithmically decreases with the coverage [4,5]:

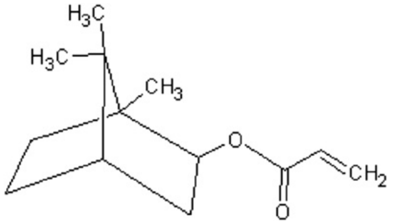
$$\theta=c_1P^{1/c2}\tag{3}$$

The aim of this work is to compare the adsorption of an epoxy acrylate resin of the type used for UV-cured coatings. This resin is an experimental formulation based upon a standard low molecular weight diglycidyl ether of bisphenol A (DGEBA) with acrylic functionality, but it has been only partially acrylated to ensure a degree of epoxy functionality is retained. Two different substrates are investigated: aluminium alloy treated with Alodine and the same alloy coated with Nabutan. The epoxy acrylate resin is supplied as a 50:50 mix by volume with a reactive diluent, iso-bornyl acrylate, (IBA), so that the resin can be processed readily.

The basic structure of the DGEBA is shown below:



The structure of the reactive diluent is shown below:



Information about the interactions between the resin and the substrate can be obtained by the construction of adsorption isotherms. ToF-SIMS was used to measure the uptake of the adsorbate directly from the surface of the substrate.

2. Experimental

Eight substrates of Al2219 were treated with Alodine 1200 and eight substrates of the same alloy were treated with Nabutan STI/310, using standard procedures described elsewhere [6,7]. They were then cleaned in an ultrasonic bath for 25 min in acetone and subsequently for 25 min in toluene. One of the specimens was put aside and used as a reference. Seven solutions of the mixture DGEBA/IBA in toluene were prepared by progressive dilution, with the following concentrations: 10, 2, 0.4, 0.04, 0.008, 0.0008 and 0.00016 g/L (listed in Table 1). Each specimen was immersed in different solutions for 20 min and then washed in toluene three times, each time with an immersion of 3 min, using fresh solvent for every immersion, to remove any weakly adsorbed species. The samples were then analyzed with a TOF.SIMS 5 spectrometer (IonTof GmbH, Münster, Germany) using a Bi_3^+ ion beam in the high current bunched mode of operation, which provides high spectra resolution data. The beam energy used was 25 kV, with a current of 0.17 pA and a primary ion dose density (PIDD) of 6.3×10^{11} ions/cm^2. The irradiated area was $100 \times 100\ \mu m^2$. Positive and negative ToF-SIMS spectra were acquired in the range 1–600 u. To represent the epoxy functionality the following cation was used; $C_9H_{11}O^+$ (135 u) and the negative ions employed were $C_6H_5O^-$ (93 u), $C_9H_9O^-$ (133 u), and $C_{14}H_{11}O_2^-$ (211 u). The structure of the fragments is given as insets in Figs. 4–7. These peaks are all characteristic of the DGEBA chain and are thus useful in establishing the uptake of the epoxy acrylate resin on the pretreated aluminium surfaces [8]. The intensities of such peaks, normalized to the total intensity to provide the relative peak intensity, RPI ($I_{adsorbate}/I_{tot}$), were used to build the adsorption curves, using the substrate as reference. The experimental error is ~5%. The acrylate functionalities, indicative of the iso-bornyl acrylate reactive diluent, were assessed using the following anions $C_3H_3O^-$ (55 u) and $C_5H_3O_3^-$ (111 u). The structures are shown as insets to the adsorption isotherms of Figs. 8 and 9.

Table 1
Concentrations (g/L) of the epoxy acrylate resin solutions prepared.

Solution	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Conc (g/L)	10	2	0.4	0.04	0.008	0.0008	0.00016

3. Results

Fig. 1a shows a positive SIMS spectrum, in the range 0–200 u, of Al2219 treated with Alodine 1200S after immersion in the 10 g/L solution of the epoxy resin, the fragment used for the adsorption study is highlighted. Fig. 1b and c is the high resolution spectra of the positive ion characteristic of the epoxy acrylate molecule ($C_9H_{11}O^+$) from Al2219 treated with Alodine 1200 S prior to any exposure and treated with a 10 g/L solution of the epoxy resin, respectively. It is clear that this diagnostic peak is absent from the reference substrate. Fig. 2 shows a negative SIMS spectrum in the range of 0–230 u, of Al2219 treated with Alodine 1200S after immersion in the 10 g/L solution of the epoxy resin, the characteristic fragments are highlighted. Fig. 2 b, c, and d shows high resolution regions of nominal masses 93, 133, 211 u, which encompass the regions of the fragments $C_6H_5O^-$, $C_9H_9O^-$ and $C_{14}H_{11}O_2^-$, respectively. Fig. 2e, f and g are the same regions after exposure to a 10 g/L solution of the resin, respectively. All the negative fragments chosen are absent on the reference, with the exception of $C_6H_5O^-$ (93 u), present in a very low concentration. All have a significant increase in concentration after exposure to the solutions and are thus diagnostic of the epoxy acrylate. In a similar vein, Fig. 3 shows the negative ions from a Nabutan treated aluminium substrate and the same regions containing the ions diagnostic of iso-bornyl acrylate adsorption at nominal masses 55 and 111 u, following treatment with a 0.4 g/L solution of the epoxy resin.

Fig. 4 shows the adsorption curves of the epoxy acrylate resin on Nabutan STI/310 and Alodine 1200S as indicated by the $C_9H_{11}O^+$ peak intensity, plus an indication of the level at which this fragment is detected on the reference samples. This indicates the background level counts as only one ion chosen ($C_6H_5O^-$) displays a discrete peak on the reference substrates. The relative intensity was plotted against the solution concentration. The Alodine curve shows a maximum at low concentration but then develops the expected plateau, indicative of chemisorption, whilst the Nabutan curve shows a more complex behaviour: it increases at first, reaches a maximum, exhibits a decrease and increases again without reaching a plateau in the concentration range considered. Fig. 5 displays the adsorption curves for adsorption on the two conversion coatings deduced from the intensity of the $C_6H_5O^-$ peak, plus the reference data. Both curves follow the anticipated shape for a chemisorption process. The Nabutan curve does not show the "dip" seen in Fig. 4 and this may result from the presence of this ion on the reference surface as shown in Fig. 2(b). The trend shown in Fig. 6 is similar to the data from the Alodine treated substrate but comparable to Fig. 4 for the Nabutan conversion coating. This trend is repeated in Fig. 7 for the $C_{14}H_{11}O_2^-$ ion.

The adsorption behaviour of the reactive diluent is shown in Figs. 8 and 9 using the $C_3H_3O^-$ and $C_5H_3O_3^-$ ions, respectively. In both of these curves a low level of adsorption are seen on the chromate treated aluminium substrates but a higher and more complex behaviour is seen in the case of the hybrid conversion coating. This features a gentle rise to a maximum value followed by a gradual decrease to a minimum and then a very slight rise.

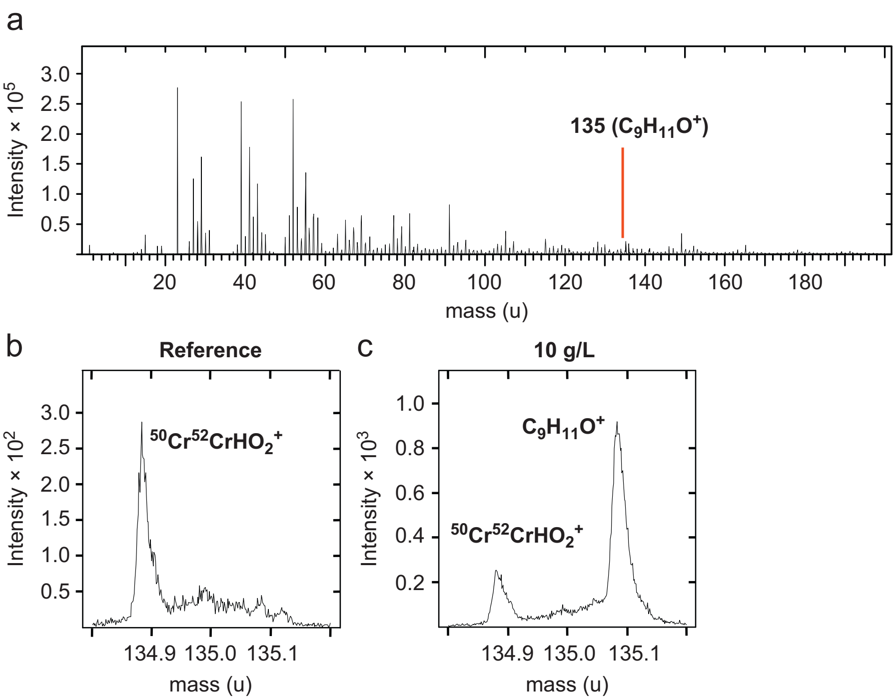


Fig. 1. (a) Positive SIMS spectrum of Al2219 treated with Alodine 1200 immersed in a 10 g/L solution of the resin (0–200 u); (b) $C_9H_{11}O^+$ region from the reference specimen; and (c) the same region after immersion in a 10 g/L solution of the epoxy resin.

The reference spectra recorded from the conversion coatings applied to the aluminium alloy prior to the adsorption of the epoxy acrylate system, show the absence of most of the fragments on the surface before the immersion in solution. The adsorption of the iso-bornyl acrylate reactive diluent is relatively small compared with the epoxy acrylate molecule on the Alodine 1200 treated substrate and for this reason it is appropriate to consider the behaviour of this system in terms of the adsorption of the DGEBA based resin. The standard test procedures [9] were used to assess the conformity of the adsorption of epoxy acrylate resin on Alodine 1200 treated Al2219 to the Langmuir (or other) models, using the all ions described above as representative of the adsorbate. The Langmuir curve, according to Eq. (1), was obtained plotting the ratio of the concentration by the relative peak intensity (c/RPI) versus solution concentration (c); the Temkin curve, according to Eq. (2), was obtained plotting the relative peak intensity (RPI) versus the natural logarithm of the solution concentration (lnc); the Freundlich curve, according to Eq. (3), was obtained plotting the natural logarithm of the relative peak intensity (lnRPI) versus the natural logarithm of the solution concentration (lnc). The more similar the adsorption process is to the ideal model, the closer the new curves will be to a straight line. The linear least squares method was used to fit the curves and the R^2 values are displayed in Table 2, which clearly indicates that using all ions considered, adsorption conforms to the Langmuir model.

A similar procedure was carried out for the resin adsorbed on the Nabutan pretreated Al2219 and, rather surprisingly, similar results are obtained as indicated in Table 3, although the linear regression fit is not as good. This result is rather unexpected as all ions, but one, characteristic of DGEBA show a “dip” at low concentrations, but it is clear that although the fit is not as good as that achieved for the epoxy base molecule the Langmuir Model is considerably better in all cases that either of the alternatives considered above.

Inspection of the behaviour of ions characteristic of the reactive diluent, Figs. 8 and 9, shows that the “dip” in the DGEBA intensity seen in Figs. 4, 6 and 7 is complemented by a concomitant rise in the reactive diluent intensity at the same concentration. It can also be seen that the data for the Alodine 1200 substrate is at a much lower intensity, reinforcing the observation, relating to the DGEBA adsorption, that the inorganic conversion coating has a much lower propensity to adsorb organic molecules than does the hybrid conversion coating. This phenomenon is thought to be important in achieving a fuller understanding of the adsorption process on this substrate and is returned to at some length below.

4. Discussion

The two conversion coatings compared in this study are very different in nature. The Alodine is an inorganic coating and its main component is chromium oxide. The Nabutan is an organic coating, a mixture of organic and inorganic acids, fluorotitanic acid being one of them [10]. It was therefore expected that they would have different adsorption behaviours. All the adsorption curves relating to the Alodine treated substrate display the same trend, with the exception of that deduced from the $C_9H_{11}O^+$ relative peak intensities. The curves obtained from the peak intensities of $C_6H_5O^-$, $C_9H_9O^-$ and $C_{14}H_{11}O_2^-$ ions exhibit a monotonic increase with a plateau, where monolayer coverage is attained. The tests for isotherm type described above, the R^2 values of which are present in Table 2, give confirmation of the very good agreement with the Langmuir model, which implies monolayer coverage and no lateral interactions. The peaks assigned to $C_9H_{11}O^+$ gives an unusual curve, which shows a maximum at the concentration 0.4 g/L, then a drop and a rise, without reaching saturation of the surface in the range considered. The curves relative to the reactive diluent on Alodine 1200 (Figs. 8 and 9) both follow the same general form, which is similar to that of ions diagnostic of the DGEBA, but at significantly lower surface concentrations. It would appear that for the inorganic conversion coating the DGEBA and reactive diluent molecules

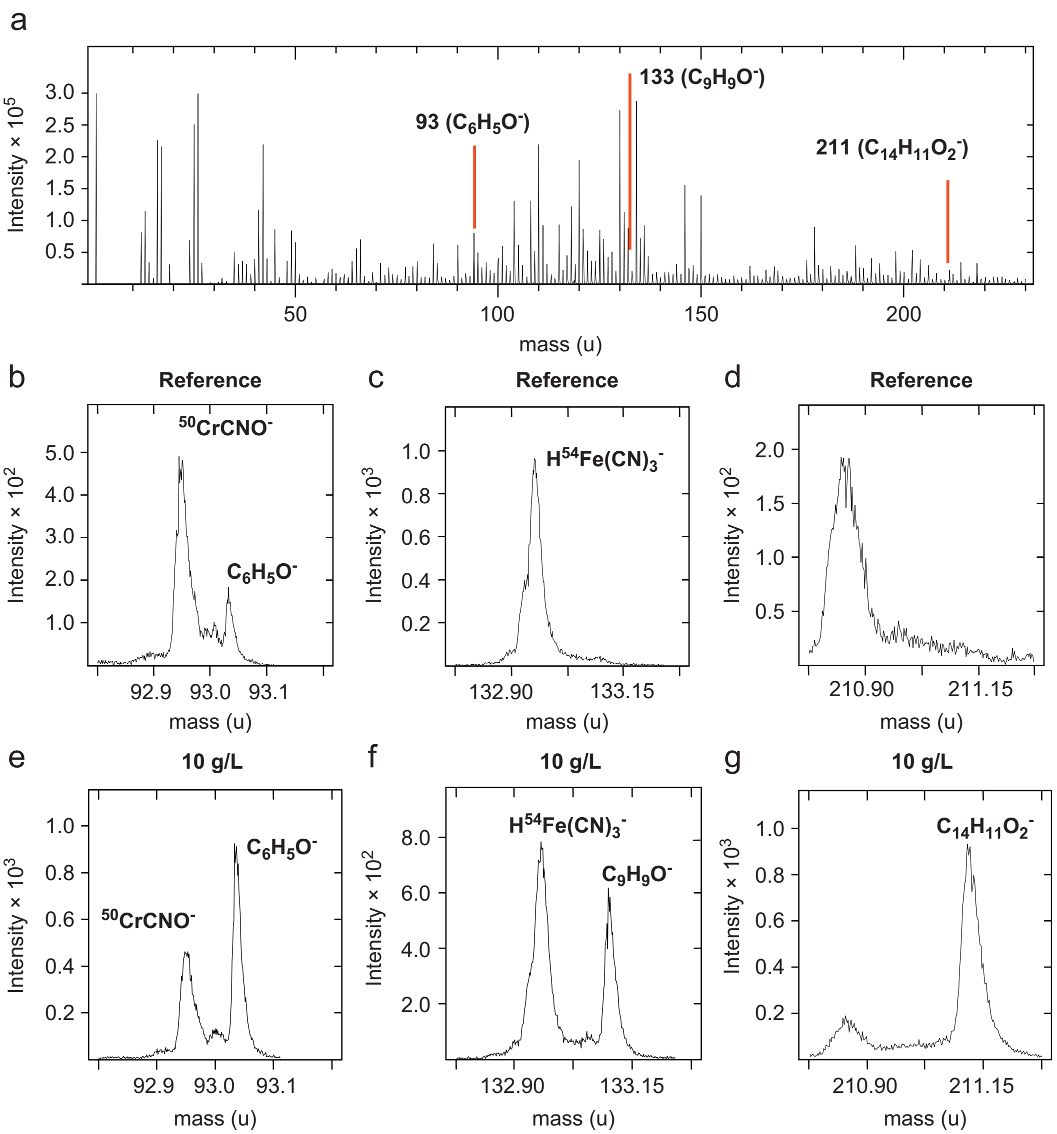


Fig. 2. (a) Negative SIMS spectrum of Al2219 treated with Alodine 1200 immersed in a 10 g/l solution of the resin (0–230 u); (b–d) $C_6H_5O^-$, $C_9H_9O^-$ and $C_{14}H_{11}O_2^-$ region from the reference specimen; and (e–g) the same region after immersion in a 10 g/L solution of the epoxy resin.

adsorb in concert, possibly by a coadsorption phenomenon. This is clearly not the case for the Nabutan treated substrates. As shown in Table 3, the Langmuir model is the one that better describes the system, although the agreement is not as good as for the Alodine 1200 substrate.

Considering firstly the ions relating to DGEBA, all the curves relative to Nabutan have the same characteristics, they do not reach saturation and they have higher RPI values than the Alodine curves. Another feature of those curves should be noticed: they all display a maximum, followed by a minimum (a "dip") at low concentrations, apart from the peak $C_6H_5O^-$. This behaviour is reminiscent of the oscillatory behaviour has been described extensively by Quinton et al. [11] and Quinton and Dastoor [12,13]. They observed the same curve pattern studying the kinetics of adsorption of organosilanes on iron and aluminium oxide surfaces and concluded that the system must be determined by two or more dynamical variables that could be the concentrations of two different adsorption species. They assumed that the two species were monomers and dimers of the compound studied and they developed a theoretical model which defines the phases of the process: a first adsorption of the monomer, up to a maximum, then its desorption by displacement (drop) and a new and slower adsorption of dimers or larger species, which would form a more stable and durable bond with the surface.

In the current study, however, the binary nature of the adsorbate solute allows the study of the behaviour of the two molecular species independently. The data of the iso-bornyl acrylate species shows quite clearly that the "dip" in the DGEBA is associated with a maximum in the reactive diluent behaviour. This points to the source of the behaviour being a competitive adsorption process between the two solute molecules in the solution [14]. The adsorption process as a function of concentration, i.e. in terms of the thermodynamics, can be considered as follows: in very dilute solutions there is a paucity of adsorbate (of both types) arriving at the substrate surface and all molecules are readily adsorbed. As the solution concentration increases so does the adsorption of both species until, at a critical concentration the IBA is adsorbed at the expense of (perhaps displacing) the DGEBA. As the solution concentration increases further the IBA is displaced by the DGEBA, which continues to increase as a function of solution concentration. The behaviour is thought to result from two properties of the adsorbing molecules, the relative concentration of functional groups and the ease with which conformational changes can occur,

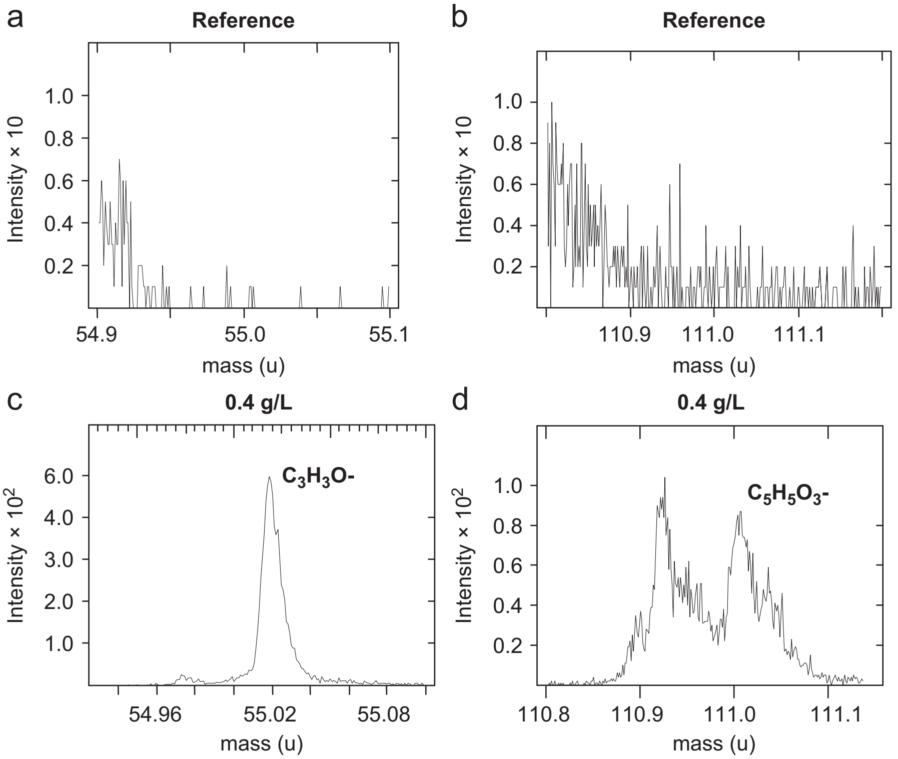


Fig. 3. Negative high resolution SIMS spectra of the peaks $C_3H_3O^-$ and $C_5H_5O_3^-$ (a, b) from Al2219 treated with Nabutan STI/310 (reference); and (c,d) after immersion in a 0.4 g/L solution of the epoxy resin.

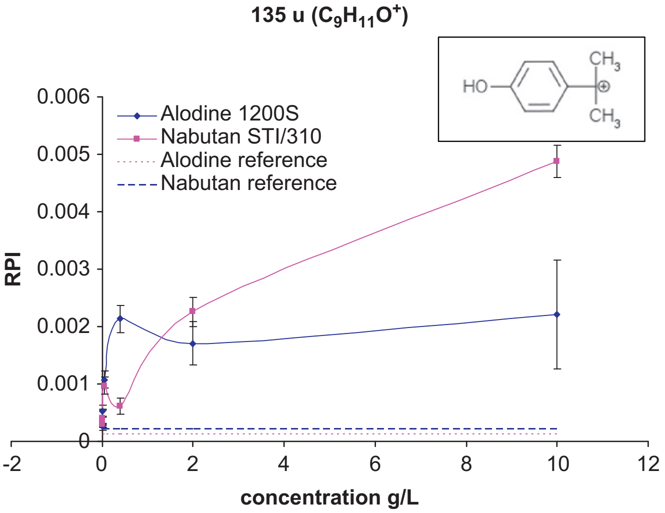


Fig. 4. Adsorption curves of Al2219 coated with Alodine 1200S (blue) and Al2219 coated with Nabutan STI/310 (pink), using the $C_9H_{11}O^+$ relative peak intensity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

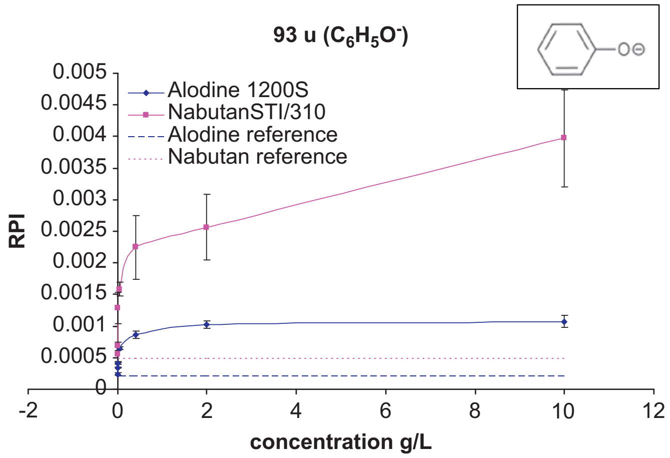


Fig. 5. Adsorption curves of Al2219 coated with Alodine 1200S (blue) and Al2219 coated with Nabutan STI/310 (pink), using the $C_6H_5O^-$ relative peak intensity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the IBA may be impeded by steric hindrance, which will not present such a problem to the more flexible, linear, DGEBA polymer. Such competition though arises with the hybrid conversion coating only, as it is singularly absent from the Alodine 1200 substrate results, meaning that the nature of the Nabutan STI/310 has also its importance in the adsorption mechanism.

In this study the use of commercial pretreatments has meant that the functionality of the substrate cannot be defined with the precision that one would ideally like to see in investigations of this type. The organic nature of the Nabutan pretreatment is expected to play an important role in the process, giving rise to undocumented interactions with the components of the resin, or even with the solvent, which is also organic in nature, and consequently increasing the number of dynamic variables in the system. For this reason the competitive adsorption process observed is also related to the heterogeneous nature of the substrate and it is inevitable that the observed behaviour reflects adsorption on both types of adsorption site.

One must also recall that the adsorbate is more correctly described as a binary mixture of the modified DGEBA and a reactive diluent.

A major difference between this study and the experiments conducted by Quinton and Dastoor is that while they monitored

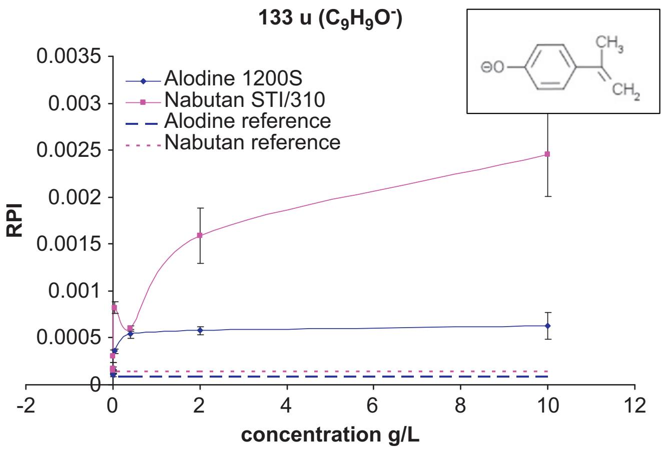


Fig. 6. Adsorption curves of Al2219 coated with Alodine 1200S (blue) and Al2219 coated with Nabutan STI/310 (pink), using the $C_9H_9O^-$ relative peak intensity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

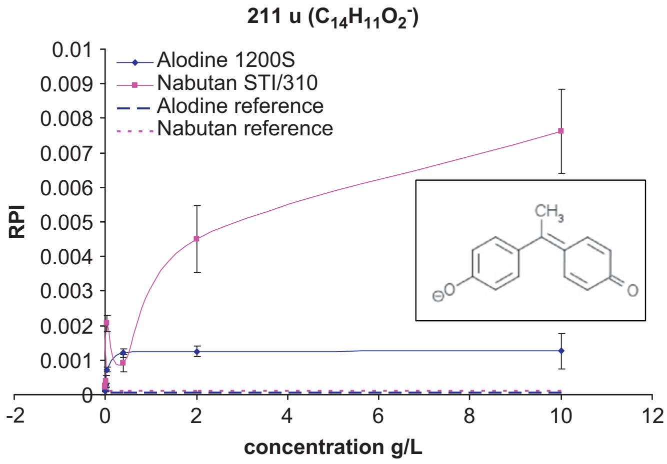


Fig. 7. Adsorption curves of Al2219 coated with Alodine 1200S (blue) and Al2219 coated with Nabutan STI/310 (pink), using the $C_{14}H_{11}O_2^-$ relative peak intensity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

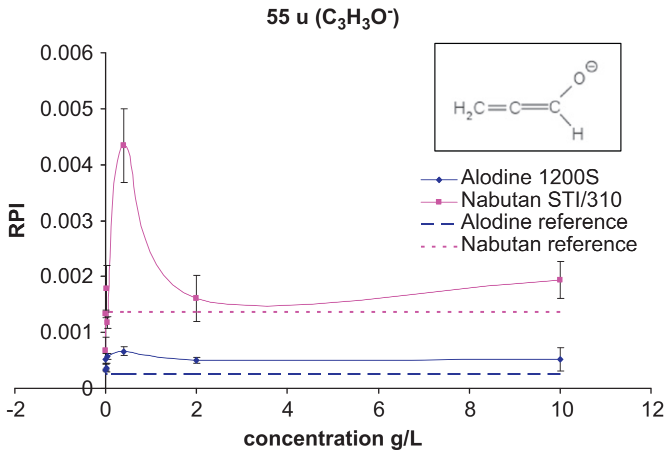


Fig. 8. Adsorption curves of Al2219 coated with Alodine 1200S (blue) and Al2219 coated with Nabutan STI/310 (pink), using the $C_3H_3O^-$ relative peak intensity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

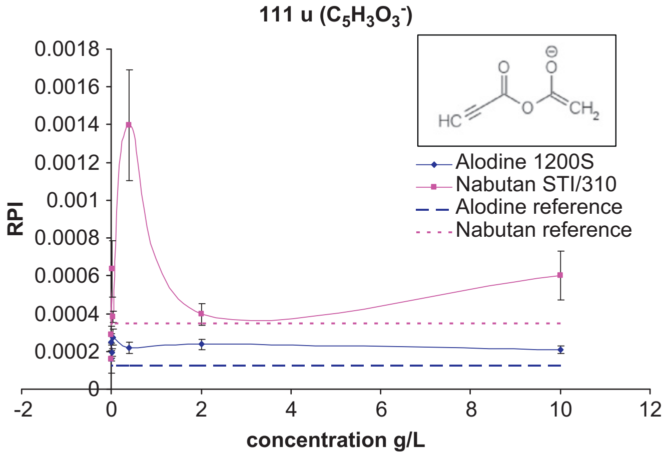


Fig. 9. Adsorption curves of Al2219 coated with Alodine 1200S (blue) and Al2219 coated with Nabutan STI/310 (pink), using the $C_5H_3O_3^-$ relative peak intensity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
R^2 of the Langmuir, Temkin and Freundlich modelled curves for the Alodine coated specimens.

Alodine 1200S	$C_6H_5^+$	$C_9H_{11}O^+$	$C_{13}H_9^+$	$C_6H_5O^-$	$C_8H_5O^-$	$C_9H_9O^-$	$C_{14}H_{11}O_2^-$
Langmuir	0.9999	0.9966	0.9977	0.9999	1	0.9997	1
Temkin	0.9387	0.8538	0.9271	0.8237	0.9233	0.8999	0.893
Freundlich	0.9697	0.9262	0.9495	0.7778	0.9298	0.9243	0.93

the kinetic behaviour (adsorption vs time), in this work the thermodynamic aspect is observed (adsorption vs concentration of adsorbate). Bearing in mind this relevant distinction, Quinton and Dastoor's interpretation of their results was useful in developing a hypothesis to explain the results presented here. Sharing the basic concept that an increased number of variables should determine the system, a more careful observation of the used substrates and adsorbate is needed to identify them. The adsorbate consists of a mixture, in equal parts by volume, of the epoxy acrylate resin based on bisphenol A and iso-bornyl acrylate. Considering the chemistry (functionality) of the two solutes it can be assumed that a small molecule from this epoxy resin would have from one to three functional groups: the epoxy group, the hydroxyl group and the carboxylic group, whereas the IBA will have the two oxygens of the ester grouping. In addition, every DGEBA molecule will have a reactive functional group at both sides of the chain, as the DGEBA is partially acrylated, there will be an epoxy group at one end and an acrylate moiety at the other. Along the chain positive and negative sites alternate at a molecular scale, providing permanent dipoles. The Alodine 1200 surface is mainly chromium oxide, so an ideal surface (not taking into account any sort of defect in the coating) consists of a matrix of Cr and O atoms that alternate in the two dimensions. Reactive sites consist of the “positive” chromium and to a lesser extent the “negative” oxygen alternating at the atomic scale as most of the organic functional groups are nucleophilic with a few electrophilic such as the electron depleted carbon of the acrylate functional groups. The Nabutan coating is a commercial treatment made of titanium dioxide, mixed with an organic polymer which is not fully defined. However it can be assumed that the surface would have well defined polarity at the molecular scale (as a result of the polymer) and at least two active sites: the

Table 3
R^2 of the Langmuir, Temkin and Freundlich modelled curves for the Nabutan coated specimens.

Nabutan STI/310	$C_6H_5^+$	$C_9H_{11}O^+$	$C_{13}H_9^+$	$C_6H_5O^-$	$C_8H_5O^-$	$C_9H_9O^-$	$C_{14}H_{11}O_2^-$
Langmuir	0.9968	0.8932	0.9902	0.9879	0.9844	0.9766	0.9094
Temkin	0.582	0.5413	0.6539	0.8608	0.734	0.7109	0.6223
Freundlich	0.6136	0.7392	0.7528	0.9606	0.908	0.9143	0.8302

titanium cation and one (or probably more) functional group from the polymer.

It is evident that the system is rather complex. In order to propose a possible behaviour mechanism, a few considerations on the adsorption curves should be made. Figs. 6 and 7 are the most reliable as they have the lower level of presence of the fragment monitored in the reference specimen (the conversion coated substrates prior to adsorption). According to the curve behaviour the concentration axis can be divided in two ranges for the Alodine and three for the Nabutan. Looking at the Alodine curves the adsorption grows monotonically in the range 0.00016–0.4 g/L, where it reaches a plateau, which extends over the range 0.4–10 g/L. This indicates that in this system there is a tendency for only one site to be active on the substrate, and probably only one active site from the adsorbate, since only the functional group with the major affinity with the Cr site will react, unless reactive sites from the adsorbate are equivalent in energy. At 0.4 g/L the surface is saturated. The Nabutan curve is more complex. It grows monotonically in the range 0.00016–0.04 g/L. At 0.4 g/L adsorption reduces, and then at 2–10 g/L it increases again, without reaching a plateau. Overall the RPI is higher than for Alodine. The higher adsorption of Nabutan may be explained by the fact that the substrate has more active sites, or greater affinity with the adsorbate, compared with the Alodine/resin system.

At low solution concentrations small molecules will freely approach the organic substrate, giving several possible interaction schemes between substrate and adsorbate so that the adsorption increases with concentration. At 0.4 g/L the adsorption of the DGEBA decreases, whilst that of the IBA increases. This implies that at this concentration it is more advantageous for adsorption of the IBA as it is a smaller, although a more rigid, molecule than the DGEBA, and attachment via the acrylate functionality is relatively straightforward. As the concentration of the solution is increased so it becomes more advantageous for the DGEBA molecules, with the plethora of bonding sites and relatively flexible molecular architecture, to adsorb on the unoccupied adsorption sites and then displace the IBA species which are tethered to the substrate via the single acrylate group. The DGEBA has potential bonding functionalities at each end of the molecule (epoxy and acrylate) as well as hydroxyl groups along the chain, thus providing more secure attachment than the single acrylate group of the IBA. In this manner the adsorption curves exemplify complementary behaviour typical of competitive adsorption. To assign the reactions responsible of the adsorption process a better understanding of the composition of the substrate is needed. This could be achieved with further studies on the organic coating. The active sites present on Nabutan could be identified using a different adsorbate, of well known composition, as a probe.

To summarize, the adsorption of two systems was studied: epoxy resin/Alodine and epoxy resin/Nabutan. The first system follows the Langmuir model closely, all sites are equivalent, there are no interactions other than the reaction between one active site from the adsorbate and one active site of the substrate and the process terminates with apparent monolayer coverage, of the substrate by both DGEBA and IBA, indicative of a coadsorption. The second system is more complex, with competitive adsorption occurring between DGEBA and IBA, most importantly the adsorption process does not terminate with monolayer coverage. This leads to a more complex behaviour where different factors become more or less relevant according to the solution concentration, and the result is an irregular adsorption pattern and a higher adsorption level.

5. Conclusions

The adsorption of an acrylate epoxy resin on coated aluminium alloy was studied at different resin concentrations. Two coatings were used, the chromium based Alodine 1200S, and the Cr-free Nabutan STI/310, containing organic components. The two coatings displayed a different behaviour, the Alodine showed a monotonic increase, reaching the monolayer coverage; while the Nabutan gave evidence of an oscillatory nature of the process and it did not reach a plateau. This difference is attributed to the organic nature of Nabutan.

In respect to the used resin the overall adsorbate concentration is higher on the Nabutan than on Alodine, probably because of the greater affinity between the polymer and the coating, being both organic compounds. The implication is that Nabutan has the potential to be a better substrate for epoxy resin based coatings. Further studies are needed to establish the reactions involved, and adsorption sites on the substrate could be identified using an adsorbate with known composition as a probe.

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