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ToF-SIMS studies of the adsorption of epoxy resin molecules on organosilane-treated aluminium: Adsorption kinetics and adsorption isotherms

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Abstract

Time of flight secondary ion mass spectrometry (ToF-SIMS) has been employed for the study of the adsorption of epoxy resin molecules, diglycidyl ether of bisphenol A (DGEBA), on aluminium substrates treated with an organosilane, γ-glycidoxypropyltrimethoxysilane (GPS). Both the kinetics of adsorption and the thermodynamics have been examined, by the construction of adsorption isotherms. The kinetics of adsorption was investigated to establish an exposure equilibrium time for DGEBA adsorption onto GPS-treated aluminium. Specimens were treated with three different concentrations of DGEBA solution and six times of treatment. It was found that DGEBA molecules were adsorbed on the aluminium substrate and reached a true adsorption equilibrium after 10 min. Adsorption isotherms were then produced to define the type of adsorption. Two possible types of adsorption isotherms, Langmuir and Temkin, were examined, and DGEBA adsorption was found to be of the Langmuir type, providing a better fit than Temkin adsorption. Using a modified form of the Langmuir equation, the fractional monolayer coverage of DGEBA molecules was determined.

Keywords: Epoxides, primers and coupling agents; Aluminium and alloys; Secondary ion mass spectrometry; Adsorption isotherms

1. Introduction

Epoxy resins based on the diglycidyl ether of bisphenol-A (DGEBA) are extensively used in adhesive bonding. During consolidation on metal or non-metal substrates, epoxy resins react with curing agents or hardeners (e.g. aliphatic or aromatic amines and/or anhydrides). This forms a crosslinked structure; a three-dimensional molecular network. The crosslinking provides a thermosetting resin and enhancement of materials properties such as low shrinkage, high strength, good chemical resistance and high electrical insulation [1,2]. Due to these excellent properties, epoxy resins have been employed for many applications, especially in the aircraft industry. In the attainment of good durability, pretreatment of the metal substrate is necessary and one evolving process is the use of an organosilane adhesion promoter. More specifically, γ-glycidoxypropyltrimethoxysilane (GPS) has potential in aerospace applications in order to replace environmentally hazardous pretreatments (i.e. etching and anodising processes involving Cr(VI) solutions) for repair purposes [3].

In an adhesive joint system, a complex interphase region consisting of aluminium oxide/silane/cured adhesive interface exists. At the aluminium oxide/silane (GPS) interface, the hydroxyl sites of the aluminium surface interact with the silanol groups of GPS to form covalent bonds [4]. In the case of the GPS/cured resin interface, there has been no direct examination of the

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interaction of a commercial epoxy resin with the silane from a surface chemistry point of view. However, recently, a fuller understanding of a model system has been reported by Abel et al. [5] using diethanolamine as a simple model of an amine crosslinked epoxy resin to mimic its interaction with GPS. It was found that there were several types of interaction formed between diethanolamine and GPS (i.e. a hydrogen bond and a covalent bond).

In the present study, the aim is to investigate the adsorption of an uncrosslinked epoxy resin, DGEBA, on oxidised aluminium treated with GPS. The analysis is carried out using time of flight secondary ion mass spectrometry (ToF-SIMS) in order to characterise the chemical groups of the DGEBA molecule present on the treated aluminium substrate. The kinetics are initially studied and this leads to the study of the thermodynamics of the process. Furthermore, the type of isotherm is identified and the fractional monolayer coverage is deduced.

2. Adsorption isotherms

Adsorption is a phenomenon, which describes the manner by which a molecule of an adsorbate forms a bond to the surface of an adsorbent. Initially, adsorption has been studied from the gas phase at a particular temperature. Gas-phase adsorption has also been used to predict the fractional monolayer coverage (θ) involved with the ratio of the number of adsorption sites occupied (N) to the total number of surface sites available (N_s) as well as the ratio, at constant pressure, of the volume of gas adsorbed (V), to the volume of gas adsorbed which corresponds to all adsorption sites being occupied (V_∞) [6].

$$\theta = \frac{N}{N_s} = \frac{V}{V_\infty}. \tag{1}$$

Adsorption is classified as being physisorption or chemisorption, depending on the bond energies or the enthalpy of adsorption. In physisorption, the bonding is associated with weak Van der Waals forces. The enthalpy of adsorption is less negative than $-25\,\mathrm{kJ\,mol^{-1}}$. In chemisorption, a chemical bond is formed between the adsorbate molecules and the adsorbent surface. Chemisorption is characterised by primary bonds (ionic, metallic, or covalent bonds) and stronger secondary bonds. The adsorption enthalpies are related to the chemical bond strength and are more negative than $-40\,\mathrm{kJ\,mol^{-1}}$ [6]. Moreover, the important difference between both physisorption and chemisorption is the restriction of the saturation uptake of the adsorbate molecules adsorbed onto the surfaces. Multilayer formation occurs in the case of physisorption whereas chemisorption is limited to a monolayer. There are several types of models to describe chemical adsorption such as Langmuir, Temkin, and Freundlich types. These isotherms are different in the assumptions shown in the derived expression for the surface coverage. Langmuir isotherm is the most simple one for the adsorption of adsorbate onto the adsorbent, which is based on several assumptions, the most important ones are as follows:

(i) Only one monolayer of an adsorbing molecule can be adsorbed on the adsorbent of the substrate.
(ii) All sites are equivalent.
(iii) The ability of a molecule to adsorb at a given site is not dependent on the occupation of neighbouring sites.
(iv) The enthalpy of adsorption is constant.

According to these assumptions, the fractional monolayer coverage at pressure, P, is defined as the following expression:

$$\theta = \frac{bP}{1+bP}, \tag{2}$$

where b is the ratio of the rate constants for adsorption and desorption. The b constant is related to both the enthalpy of adsorption and temperature. It is usually expressed as

$$b = b_0 \exp(Q/RT), \tag{3}$$

where b_0 is a pre-exponential factor, Q is the interaction energy, R is the gas constant, and T is the temperature.

When θ is replaced with V/V_∞, the rearrangement gives the following expression:

$$\frac{P}{V} = \frac{1}{bV_\infty} + \frac{P}{V_\infty}. \tag{4}$$

As indicated above, Langmuir adsorption isotherm assumes independence and equivalence of adsorption sites. These assumptions will fail if there is a difference in the enthalpy of adsorption for different sites. Sites which are more energetically favourable are occupied initially as a result of having more negative adsorption enthalpy. This indicates that the enthalpy of adsorption will change as a function of θ. Hence, two types of isotherms were developed. Firstly, the Temkin isotherm assumes that the enthalpy of adsorption changes linearly with gas pressure. This isotherm is expressed as

$$\theta = C_1 \ln(C_2 P), \tag{5}$$

where C_1 and C_2 are constants.

Secondly, the Freundlich isotherm assumes that the adsorption enthalpy of this type varies logarithmically with gas pressure. It is simply given by

$$\theta = C_1 P^{1/C_2}, \tag{6}$$

where C_1 and C_2 are constants.

The study of adsorption from the gas phase has been well understood and described in the literature but the study of adsorption from liquid phase by the analysis of the adsorbent surface following adsorption was initially reported for the adsorption of organosilane adhesion promoters onto an iron surface, by the use of X-ray photoelectron spectroscopy (XPS) [7]. Bailey and Castle showed that the adsorption of vinyl triethoxysilane was of the Temkin type and that silanes could be displaced from the iron substrate by lead and tin impurities in the solvent. Recently, the study of the adsorption from the liquid phase using surface analysis techniques, XPS and ToF-SIMS, has been reviewed by Watts and Castle [8]. In the current paper, ToF-SIMS is used to determine the adsorption isotherms. The expression of Langmuir isotherm type is traditionally related to the gas pressure in the gas phase whereas, in our approach, it is concerned with the concentration of the solution in the liquid phase that is adsorbed at the solid surface. It is this latter quantity that is measured directly in our approach. The adsorption isotherm is constructed as measuring the relative peak intensity (RPI) of a characteristic ion in the SIMS spectrum. RPI is also proportional to the fractional monolayer coverage (θ) and it is expressed by

$$\mathrm{RPI} = \frac{I_{\mathrm{ads}}}{I_{\mathrm{ads}} + I_{\mathrm{sub}}}, \tag{7}$$

where I_{ads} is the intensity of an ion in positive or negative ToF-SIMS spectrum characteristic of the adsorbate, and I_{sub} is the intensity of an ion in the same spectrum characteristic of the substrate. The use of this form of RPI for the construction of an adsorption isotherm was initially introduced by Abel et al. [9] and has been discussed at length by Vickers et al. [10].

In this work, however, RPI cannot be calculated as given in Eq. (7). As aluminium is used as the substrate and the fragment which is indicative of aluminium is $m/z = 27$ Da in the positive mode of detection. But this particular mass can also originate from a hydrocarbon fragment of GPS or DGEBA, and/or contamination: $C_2H_3^+$. Thus, RPI is calculated from the intensity of all ions, $I_{\mathrm{total\ counts}}$. The equation is written as

$$\mathrm{RPI} = \frac{I_{\mathrm{ads}}}{I_{\mathrm{total\ counts}}}, \tag{8}$$

where $I_{\mathrm{total\ counts}}$ is the intensity of all ions in the same spectrum in the mass range of 5 to 300 Da (mass veto = 0–5 Da).

The adsorption isotherm is presented by a correlation between the concentration of the adsorbate in solution, C, and the surface composition following adsorption, RPI. The Langmuir equation for the liquid-phase adsorption determined by direct analysis of the adsorbed species on the solid surface by ToF-SIMS can be written as follows [10]:

$$\frac{C}{\mathrm{RPI}} = \frac{1}{b\Omega_{\mathrm{r}}} + \frac{C}{\Omega_{\mathrm{r}}}, \tag{9}$$

where Ω_{r} is the equilibrium coverage, measured by ToF-SIMS.

The Temkin equation for the liquid-phase adsorption is expressed as follows:

$$\mathrm{RPI} = b \ln C. \tag{10}$$

Practically, even though there are several types of isotherms, Langmuir and Temkin adsorption isotherms are recommended because of the most extensive use of the Langmuir equation in surface analysis [8–12] and the initial presentation of the modified Temkin type by Bailey and Castle [7].

3. Experimental

3.1. Specimen preparation

Aluminium sheets of high purity (99.0%) were supplied by Goodfellow Cambridge Ltd. According to the standard industrial procedure [3], aluminium sheets were cleaned with detergent and tap water. After drying, aluminium samples were then grit-blasted with 50 μm fresh alumina grit (supplied by Abrasive Developments Ltd.). Samples were punched to discs of 10 mm diameter and followed by degreasing with acetone or 2-propanol to remove the contaminants obtained from grit-blasting and the punch. Samples were then brushed for 2 min with a 1% aqueous solution of GPS (OSI Silquest, product designation A187) that had been hydrolysed for 60 min for full hydrolysis in reverse osmosis, deionised and carbon-filtered water. The samples were then dried at 93 °C in an oven for 60 min.

3.2. Preparation of the DGEBA solution

DGEBA (trade name Shell Epikote 828) was supplied by Shell. 86% of the supplied DGEBA has a degree of polymerisation (n) equal to 0 (which has the relative molar mass or RMM of 340 g mol^{-1}) and 14% of this DGEBA has n equal to 1 (which has the RMM of 624 g mol^{-1}). An average relative molar mass of the DGEBA used in this experiment is thus approximately 380 g mol^{-1}. The molecular structure of DGEBA is shown in Fig. 1.

The treatment of DGEBA on the aluminium substrates coated with GPS is divided into two essential steps. The first step is the study of the kinetics of adsorption in order to investigate the exposure time to reach a true equilibrium of adsorption. The second step is the study of adsorption isotherms, to provide the saturation uptake and also define the type of adsorption.

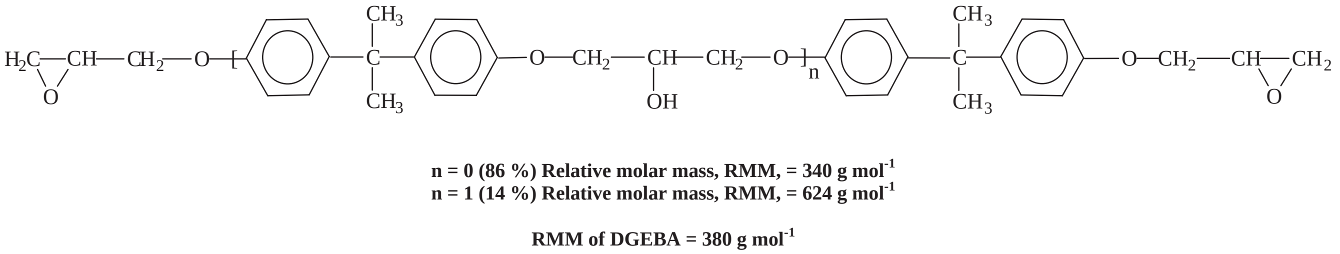


Fig. 1. Molecular structure of DGEBA.

3.2.1. Kinetic studies

A 1×10^{-1} M stock solution of DGEBA was prepared by dissolving 9.5 g of the resin in toluene in a 250 cm^3 volumetric flask. The solutions of the appropriate concentration were diluted from this stock solution. To study the kinetics of adsorption, 1×10^{-3}, 1×10^{-2}, and 1×10^{-1} M solutions of DGEBA in toluene were prepared. GPS-treated samples were immersed in these DGEBA solutions for 0.5, 1, 5, 10, 20, and 30 min. The samples were immediately rinsed with 40 cm^3 of fresh toluene three times (2 min for each rinse). All specimens were then left to dry in air for at least 30 min.

3.2.2. Thermodynamic studies

Solutions of the following concentrations: 1×10^{-3}, 5×10^{-3}, 1×10^{-2}, 5×10^{-2}, and 1×10^{-1} M of DGEBA in toluene were prepared for adsorption studies. GPS-treated samples were dipped in these solutions for 10 min. This treatment time was established from the initial kinetic study as shown below. After being treated with solutions of DGEBA, specimens were then rinsed by the same process as that employed for the kinetic study.

4. ToF-SIMS analysis

ToF-SIMS analysis was achieved using a VG Scientific type 23 system. This instrument is equipped with a double stage reflectron time-of-flight analyser and a Gallium pulsed liquid-metal ion source. Static SIMS conditions with total ion dose less than 1×10^{13} ions cm^{-2} analysis^{-1} were employed using a pulsed (10 kHz and ca. 30 ns) 20 keV $^{69}Ga^+$ primary ion beam rastered over a frame area of $500\times500\,\mu m^2$ at 50 frames s^{-1}. SIMS spectra were acquired over a mass range of 5–600 Da in both the positive and negative ion modes. All analyses were carried out in triplicate.

5. Results and discussion

Figs. 2a–d show the positive ToF-SIMS spectra ($m/z = 0$–300 Da) for (a) aluminium treated with GPS only, (b) GPS and then with DGEBA solution for 10 min at 1×10^{-3} M (c) 1×10^{-2} M, and (d) 1×10^{-1} M, respectively. Fragments of the sample treated with GPS only are assigned and shown elsewhere [4,13,14]. Some fragments such as $^{23}Na^+$ and $^{40}Ca^+$ are obtained from the grit used for the grit-blasting process. The actual composition of oxides in the grit concentration is presented in Table 1. Mass 27 is mainly assigned to Al^+ ion, which is characteristic of the substrate surface as indicated by its high intensity relative to $m/z = 29$ Da ion characteristic of $C_2H_5^+$. Also, the presence of this mass can be from a hydrocarbon fragment ($C_2H_3^+$) of GPS or DGEBA and/or contamination. The ion at $m/z = 28$ Da is partly assigned to Si^+ or $C_2H_4^+$. The appearance of some fragments (i.e. $m/z = 77$, 91, 105, 115, 121, 133, and 149 Da) is from a phthalate compound as described by Abel et al. [5] from a plasticiser leached from the water container.

Compared with the spectrum for the sample treated with GPS only, the spectra for samples treated with GPS then DGEBA, as shown in Fig. 2b–d, present most of the fragments indicative of DGEBA molecules such as $m/z = 31$, 57, 77, 91, 135, and 191 Da. All characteristic fragments of DGEBA are listed in Table 2 with their respective assignments. Mass 31 is assigned to CH_2OH^+, obtained by breaking the molecular chain of either DGEBA or GPS. It is also obvious that in the higher mass range between $m/z = 240$ and 300 Da, there are three key fragments, at nominal mass $m/z = 252$, 253, and 269 Da. Interestingly, these fragments show a high intensity in the spectra when samples are treated with 1×10^{-2} and 1×10^{-1} M solutions of DGEBA but not when treated with 1×10^{-3} M DGEBA. The correlation between the RPI and solution concentrations was investigated as shown in Table 3. It is found that the DGEBA uptake increases with increasing solution concentrations. Even though the data were not presented for the DGEBA peaks at $m/z = 252$, 253, and 269 in Table 3, their intensities also increase with increasing concentration.

Fig. 3 shows the negative ToF-SIMS spectra ($m/z = 0$–300 Da) for samples treated with GPS only and treated with GPS then three concentrations of DGEBA solution at 10 min exposure time. Fragments at

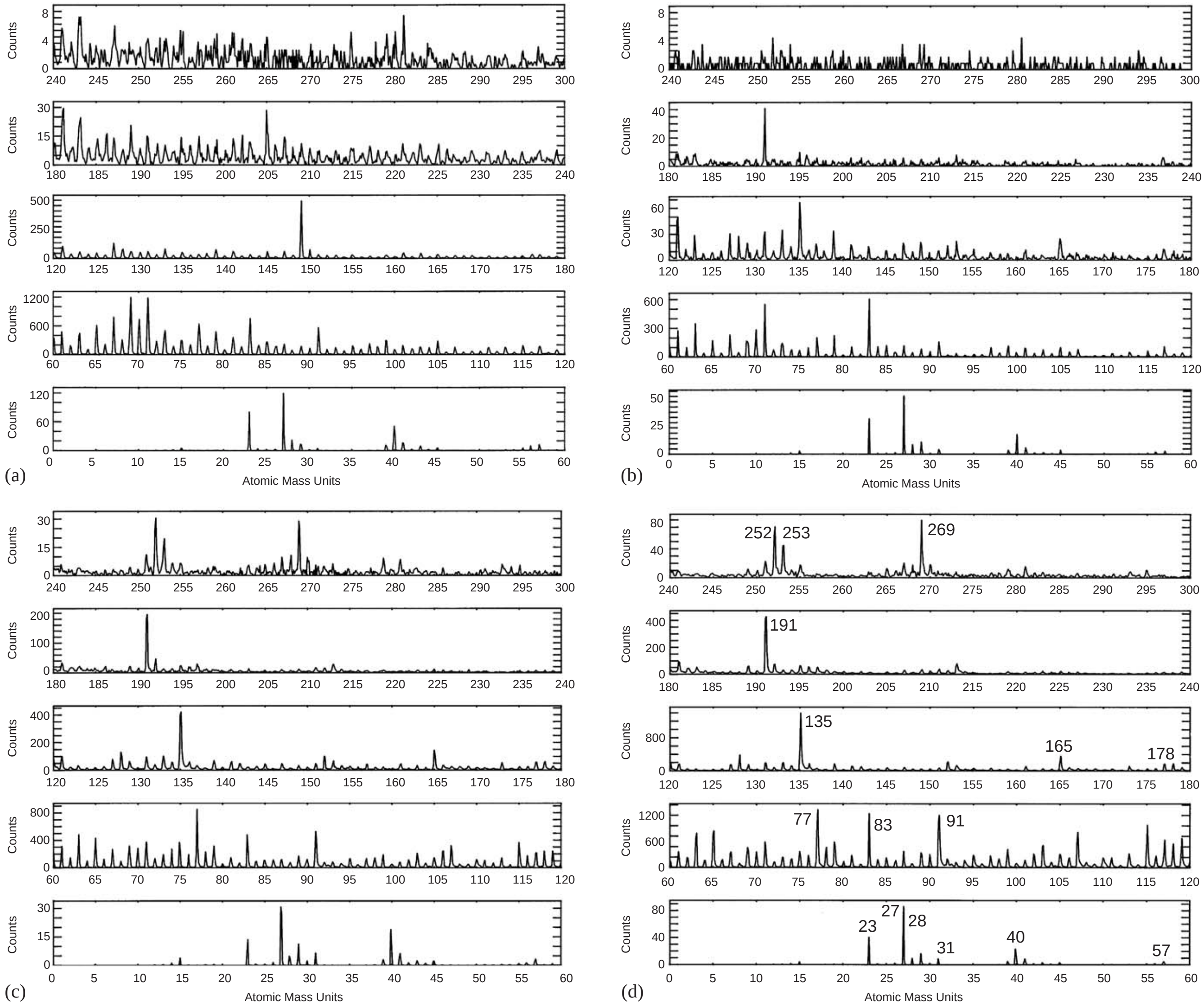


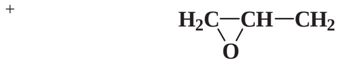
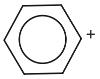
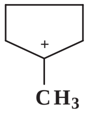
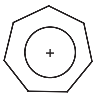
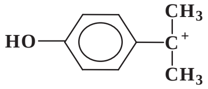
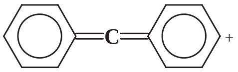
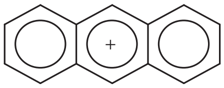
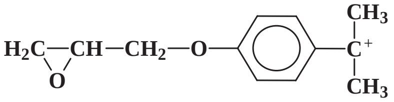
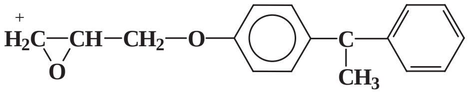
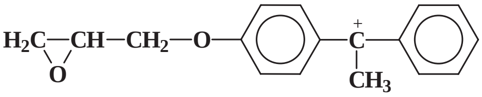
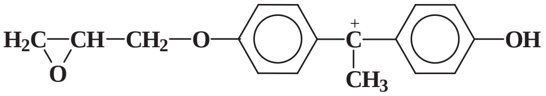
Fig. 2. Positive ToF-SIMS spectra ($m/z = 0$–300 Da) for (a) aluminium treated with GPS only, (b) aluminium treated with GPS then 1×10^{-3} M DGEBA for 10 min, (c) aluminium treated with GPS then 1×10^{-2} M DGEBA for 10 min, and (d) aluminium treated with GPS then 1×10^{-1} M DGEBA for 10 min.

Table 1
Composition of the grit-blasting medium

Materials	Bulk concentration (wt%)
Al_2O_3	Balance
SiO_2	0.02
Fe_2O_3	0.03
TiO_2	0.01 maximum
CaO	0.01
Na_2O	0.2
K_2O	0.01 maximum

16 and 17 are assigned to oxygen ion (O^-) and hydroxide ion (OH^-), respectively. Negative ions obtained from fragmentation of the GPS structure and crosslinked GPS molecules are discussed elsewhere [13,14]. For the samples treated with GPS and DGEBA, some characteristic fragments of the DGEBA molecule are identified such as $m/z = 133$, 179, and 211 Da. Besides these fragments, another main feature is seen to be indicative of DGEBA. It is the fragment at mass 283. However, this peak was hardly noticeable in the negative ToF-SIMS spectra shown in Fig. 3b for a sample treated with 1×10^{-3} M solution of DGEBA as well as peaks 252, 253, and 269 were not found in the positive spectra for the same sample. But these fragments clearly appeared when the samples were treated with 1×10^{-2} and 1×10^{-1} M DGEBA (shown in Fig. 3c and d). The assignment of negative fragments is shown in Table 4.

Table 2
Positive ion fragments for sample treated with GPS and then DGEBA

m/z	Formula	Structure
23	Na^+	
27	Al^+ / $C_2H_3^+$	
28	$^{28}Si^+$ / $C_2H_4^+$	
31	CH_2OH^+	$HO{-}CH_2^+$
57	$C_3H_5O^+$	
77	$C_6H_5^+$	
83	$C_6H_{11}^+$	
91	$C_7H_7^+$	
135	$C_9H_{11}O^+$	
165	$C_{13}H_9^+$	
178	$C_{14}H_{10}^+$	
191	$C_{12}H_{15}O_2^+$	
252	$C_{17}H_{16}O_2^+$	
253	$C_{17}H_{17}O_2^+$	
269	$C_{17}H_{17}O_3^+$	

5.1. Kinetics of adsorption

Although there are several characteristic fragments of the DGEBA molecule, only six fragments (at $m/z = 31$, 57, 77, 91, 135, and 191 Da) were employed to investigate the kinetics of adsorption, as a result of the clarity of these features in the spectra. Kinetic studies were achieved by plotting RPI as a function of time in order to obtain the adequate time to reach an adsorption equilibrium.

Fig. 4 shows the kinetic data of adsorption of DGEBA on GPS-treated aluminium. Within each curve of Fig. 4, the error bars are shown as the standard deviation of RPI. It should be noted that, for curves except that for peak $m/z = 31$ Da, the intensity of every peak is increasing versus the DGEBA concentration. The sample treated with 1×10^{-1} M solution of DGEBA exhibits the highest intensity whereas sample treated with 1×10^{-3} M exhibits the lowest intensity. At Fig. 4a for fragment 31, the intensity from the sample treated with the 1×10^{-2} M DGEBA solution is greater than that from the sample treated with 1×10^{-1} and 1×10^{-3} M, respectively. The ion of mass 31 is assigned to CH_2OH^+. This assignment may be obtained not only by fragmentation of the adsorbed GPS molecule but also by fragmentation of the DGEBA molecule. When the sample is treated with GPS, and then the least concentrated solution of DGEBA, it can be assumed that the DGEBA molecules adsorb on the GPS-coated aluminium in a patchy manner or at least with a parallel

Table 3
Relative intensity of some positive fragments characteristic of DGEBA for samples treated with three different DGEBA solutions at 10 min exposure time

Concentration of DGEBA (M)	Relative peak intensity (× 1000)			
	57	77	91	135
1×10^{-3}	23.0	1.7	1.5	0.8
1×10^{-2}	25.6	3.4	3.6	3.3
1×10^{-1}	28.5	6.7	6.8	8.6

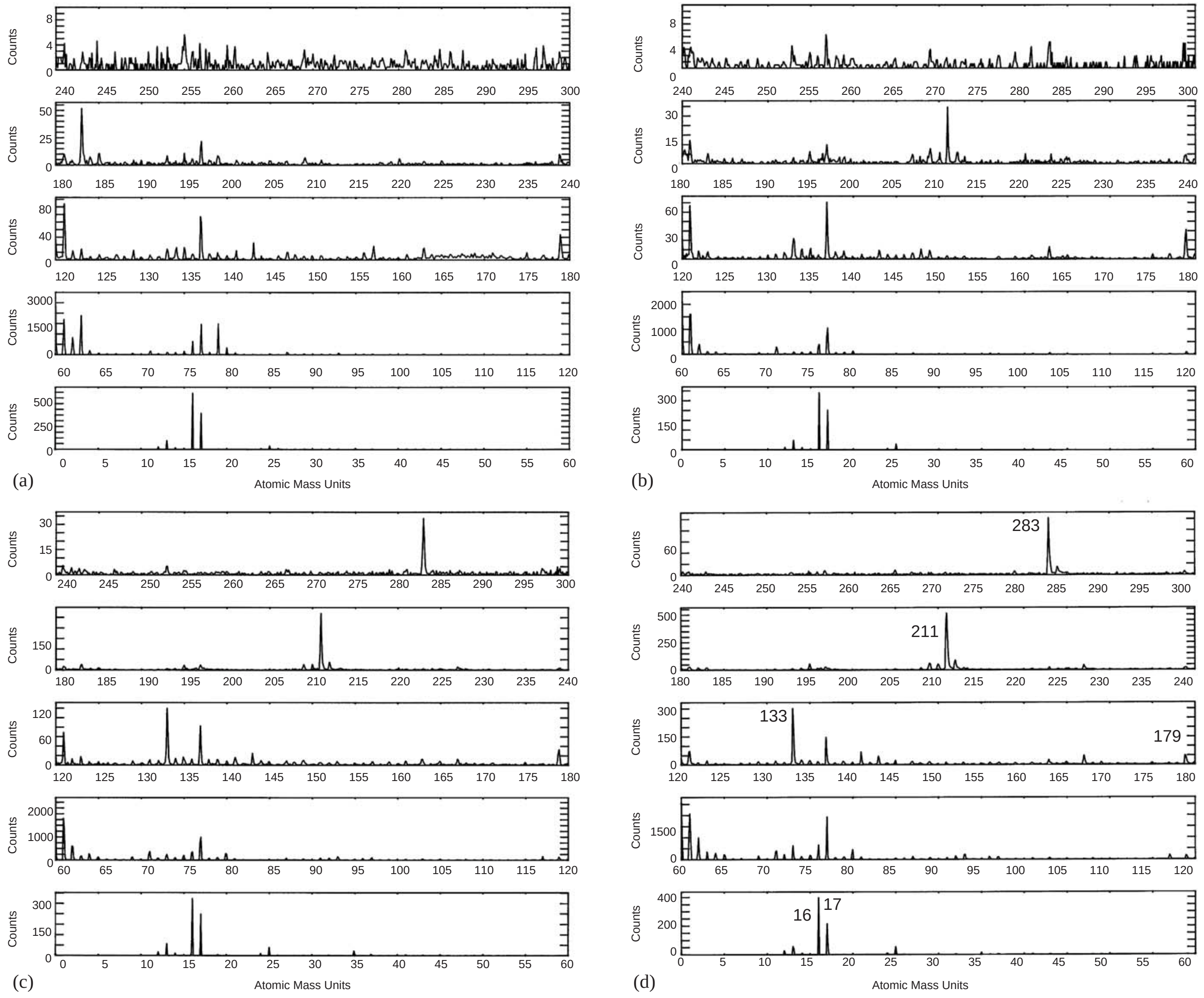
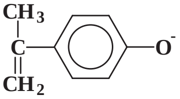
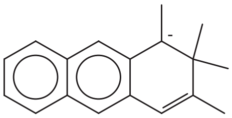
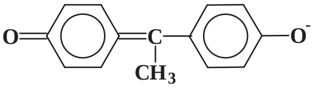
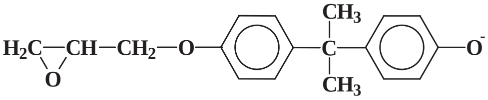


Fig. 3. Negative ToF-SIMS spectra ($m/z = 0$–300 Da) for (a) aluminium treated with GPS only, (b) aluminium treated with GPS then 1×10^{-3} M DGEBA for 10 min, (c) aluminium treated with GPS then 1×10^{-2} M DGEBA for 10 min, and (d) aluminium treated with GPS then 1×10^{-1} M DGEBA for 10 min.

Table 4
Analysis of negative ion fragments of DGEBA structures

m/z	Formula	Structure
133	$C_9H_9O^-$	
179	$C_{14}H_{11}^-$	
211	$C_{14}H_{11}O_2^-$	
283	$C_{18}H_{19}O_3^-$	

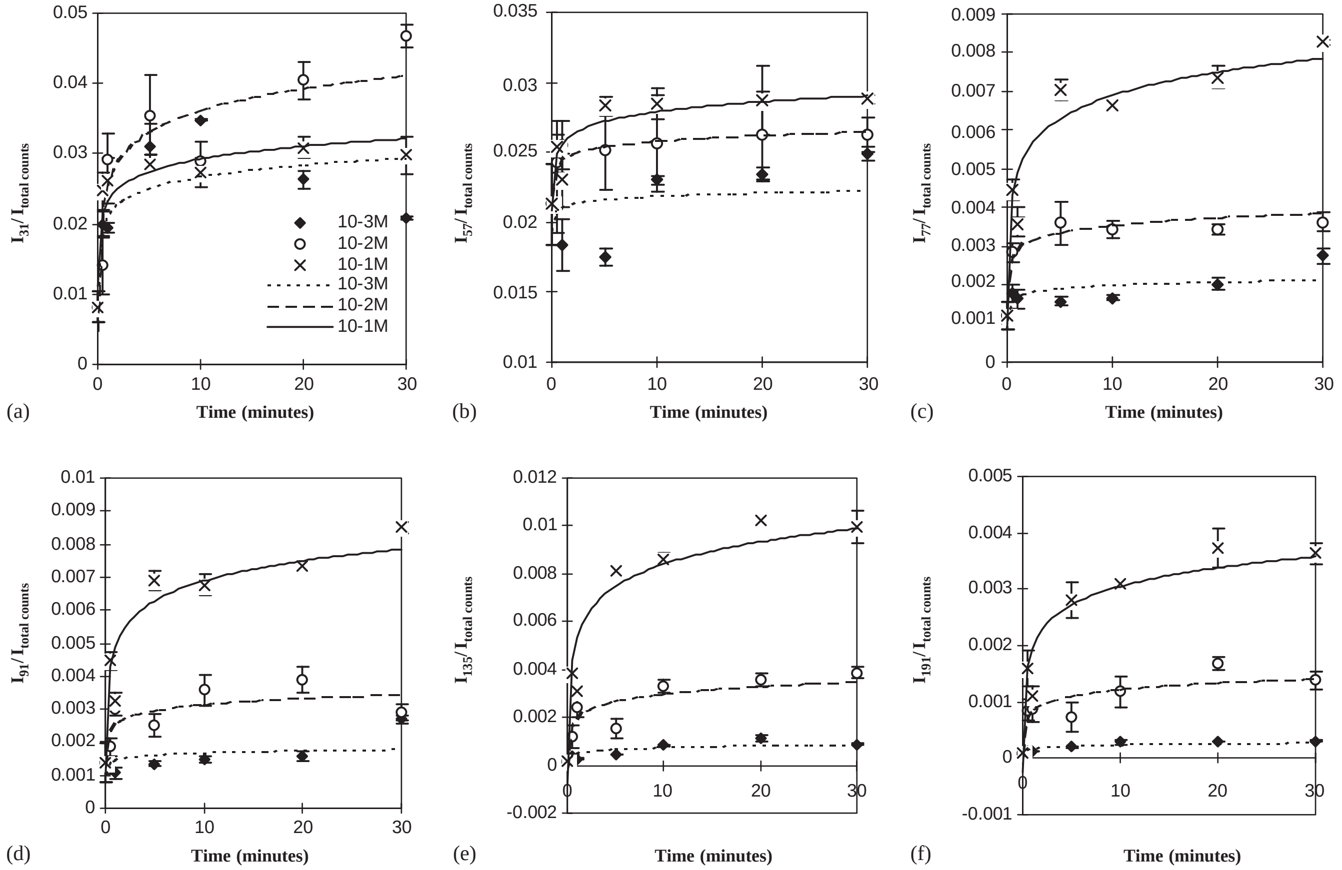


Fig. 4. Kinetic studies of DGEBA adsorption on GPS-treated aluminium, using the positive ion fragments at mass (a) 31, (b) 57, (c) 77, (d) 91, (e) 135, and (f) 191.

conformation. After being bombarded with the gallium primary ion beam, both GPS and DGEBA molecules can produce CH_2OH^+ ions. XPS analysis of similar samples confirms this conclusion [14]. The attenuation of the substrate signal by the DGEBA overlayer is minimum as indicated by XPS. Indeed, the Al2p signal is seen to increase, compared with the GPS-treated aluminium, as a result of the displacement of adventitious hydrocarbon layer by the DGEBA solution. Therefore, in this case, $m/z = 31$ Da is considered less characteristic of the adsorbed DGEBA molecules than the other molecular fragments quoted above. Fig. 4b shows the kinetic data obtained from the fragment at $m/z = 57$ Da, assigned to the epoxy group. This functional group is indicative of either a GPS or a DGEBA molecule. Thus, mass 57 is less characteristic of DGEBA when compared with mass 77, 91, 135, and 191. It is noticeable from the larger error bars shown in Fig. 4b. However, the intensity of $m/z = 57$ Da increases versus DGEBA concentration. This implies that this ion is more characteristic of DGEBA than that at $m/z = 31$ Da. From all these data, it is important to note that each curve reaches a plateau region after 10 min. It is an indication that a 10 min adsorption time was sufficient to reach an adsorption equilibrium. This time was therefore chosen for the thermodynamic investigation of adsorption as described below.

5.2. Adsorption isotherms

As described above, mass 31 is less characteristic of a DGEBA molecule than the others. Therefore, only five fragments were employed to study the adsorption isotherms. The plot of RPI (Eq. (8)) against the concentration of DGEBA solutions was constructed, corresponding to the adsorption isotherms as presented in Fig. 5 for the ions of m/z (a) 57, (b) 77, (c) 91, (d) 135, and (e) 191 Da, respectively. From these graphs, it is seen that the intensity of each particular curve rises with the solution concentration. The uptake reaches a plateau value and does not increase linearly as a function of DGEBA concentration. This is typical of chemisorption [6]. It should be noted that for all characteristic ions in the isotherms of Fig. 5 the data points at the highest solution concentration exhibit a positive deviation from the expected trend (indicated by the solid line). This is ascribed to a change in the conformation of the adsorbed molecules as described by Watts et al. [12]. The adsorption plateau lines of the curves are given at the concentration of DGEBA equal to 5×10^{-2} M. This critical point is defined as the saturation adsorption of DGEBA molecules on GPS-coated aluminium.

Bailey and Castle [7] initially studied the adsorption isotherms of organosilanes onto hydrated iron surfaces by XPS. This adsorption was described by the Temkin isotherm. In recent years, the adsorption of organic molecules onto solid substrates has been extensively investigated using XPS and ToF-SIMS [9–12]. The adsorption of those molecules onto the substrates was of the Langmuir type. In this work, ToF-SIMS analysis was employed to construct the adsorption isotherms for the uptake of DGEBA onto GPS-treated aluminium substrate using Langmuir and Temkin equations. In the case of the Langmuir isotherm, the graph is obtained by plotting the ratios of the concentration of DGEBA to RPI, (C/RPI) against the DGEBA concentration (C) as

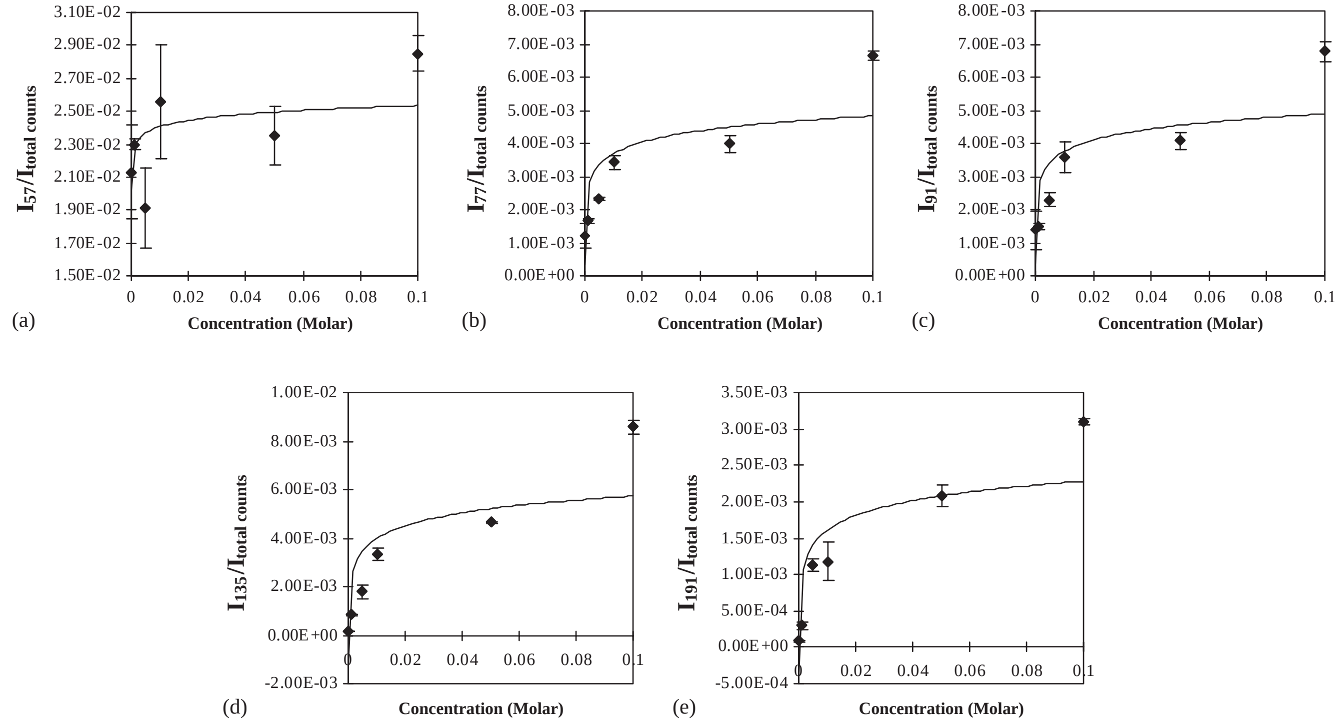


Fig. 5. Adsorption isotherms of DGEBA on GPS-treated aluminium, using the fragments at mass (a) 57, (b) 77, (c) 91, (d) 135, and (e) 191.

given in Eq. (9). Fig. 6 shows the Langmuir plots whereas Fig. 7 represents the Temkin curves constructed by plotting the RPI as a function of the natural logarithm of concentration (ln *C*) as referred to in Eq. (10). Both Langmuir and Temkin plots were fitted with a linear line and the corresponding least square value (R^2) was obtained. The least square data obtained from the Langmuir and Temkin plots are compared in Table 5. It is found that the R^2 for the Langmuir plots are indeed very close to 1 (>0.9) whereas the R^2 values for the Temkin isotherm are approximately 0.7. This shows that the Langmuir model gives a better fit than Temkin form. Even if the data points at a concentration of 0.1 M are excluded, for the reasons discussed above,

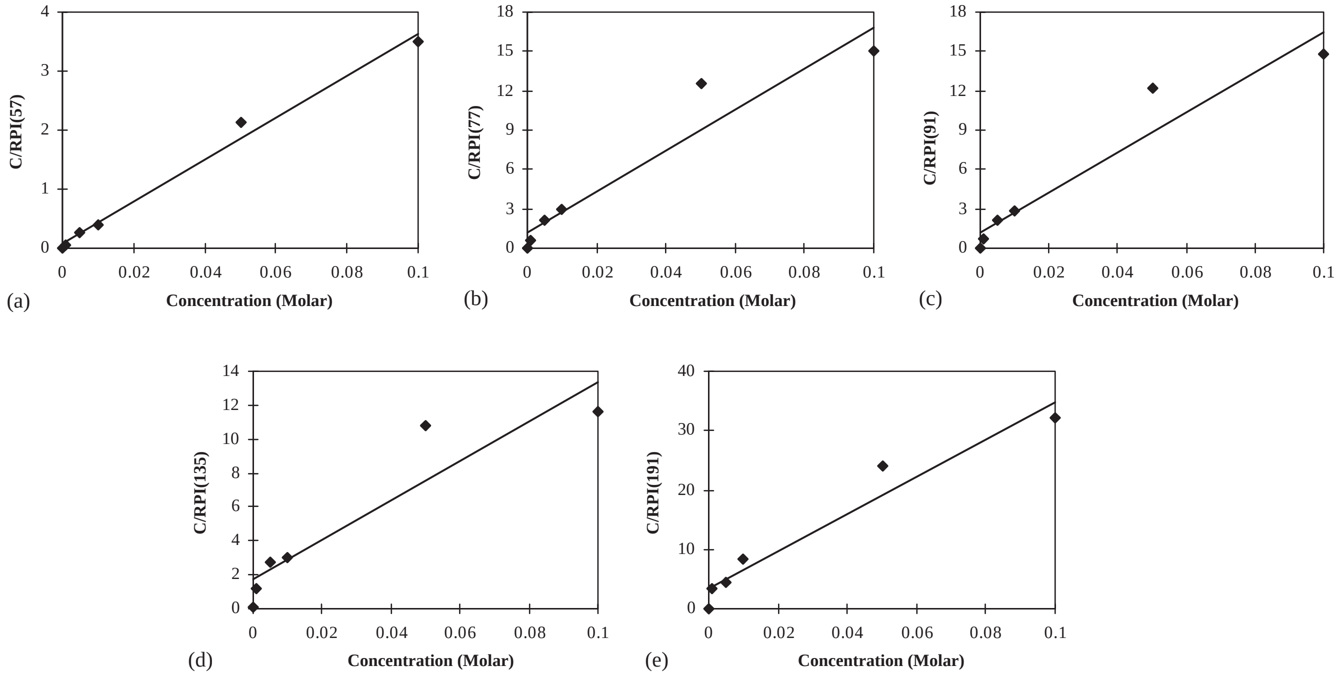


Fig. 6. Langmuir plot of the positive ion fragments at mass (a) 57, (b) 77, (c) 91, (d) 135, and (e) 191.

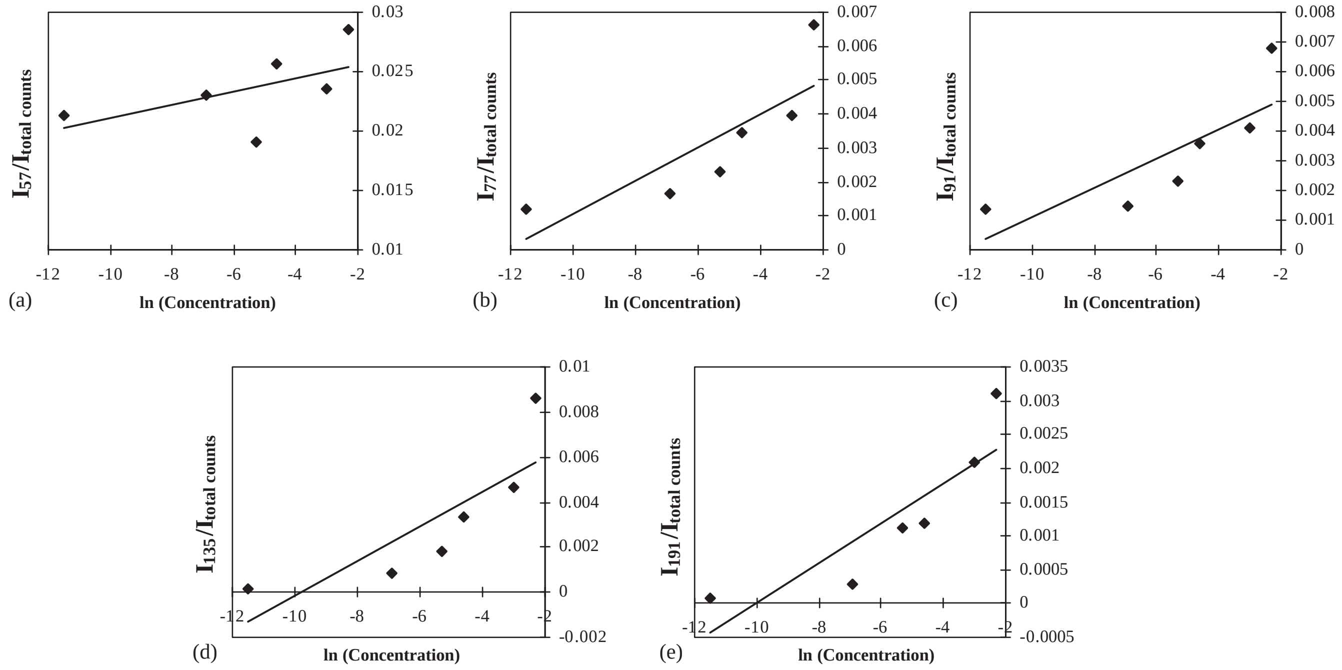


Fig. 7. Temkin plot of the positive ion fragments at mass (a) 57, (b) 77, (c) 91, (d) 135, and (e) 191.

Table 5
Comparison of the least square values (R^2) of characteristic ions to Langmuir and Temkin plots

m/z	R^2	
	Langmuir plot	Temkin plot
57	0.99	0.32
77	0.92	0.68
91	0.92	0.64
135	0.87	0.67
191	0.95	0.75

Table 6
b values calculated from the equilibrium coverage values (Ω_r) from the Langmuir plots

m/z	Ω_r ($\times 10^{-3}$)	B	Average b
57	30.0	358.0	
77	6.4	129.8	104.4 ($\sigma = 23.5\%$)
91	6.5	127.1	
135	8.6	68.4	
191	3.2	92.5	

the Temkin fit is not improved. Hence, the uptake of DGEBA on GPS-treated aluminium is of the Langmuir type. Based on the assumptions of a Langmuir isotherm, the DGEBA molecules are adsorbed on the aluminium adsorbent as a monolayer, all sites of aluminium substrate are also equivalent and independent, and the adsorption enthalpy is constant. In adhesion research, we believe that it is the first time that an investigation of epoxy resin adsorption on aluminium has been studied by comparison of adsorption data to both Langmuir and Temkin forms of adsorption. According to recent studies, many researchers have reported information about the interaction of organic molecules on various substrates by only Langmuir adsorption [9,11,12]. For example, Abel et al. [9] initially studied the adsorption of polymethylmethacrylate (PMMA) onto conducting hydrogenosulfate-doped polypyrrole ($PPyHSO_4$) in $CHCl_3$ and CCl_4 solvents. The Langmuir equation modified for ToF-SIMS analysis led to the determination of the equilibrium constant, b. The importance of the b constant was taken as an indication of the strength of bonding occurring between PMMA and $PPyHSO_4$ from $CHCl_3$ and CCl_4 solvents. It was considered that the greater b gives the stronger bond. Later, Vickers et al. [11] investigated the adsorption of organic molecules such as PMMA, DGEBA, and amine curing agent onto untreated and electrochemically oxidised carbon fibre reinforced polymer or CFRP. This investigation was achieved using ToF-SIMS. The results showed that the uptake of these three molecules on both treated and oxidised carbon fibres was of the Langmuir type. Furthermore, Watts et al. [12] studied the adsorption of PMMA on oxidised silicon and aluminium substrates using monochromated XPS. This was to understand the type of bond formed between PMMA molecule and the substrates. Langmuir isotherm was the best manner to describe the PMMA uptake onto both oxidised silicon and aluminium surfaces, and linked to the surface coverage determination.

Referring to Eq. (9), the Langmuir plots were made by plotting C/RPI against C. The graphs showed a simple linear line, which gave the slope, $1/\Omega_r$, and the y-axis intercept, $1/b\Omega_r$. The b value, determined as the ratio of the rate constant for adsorption (k_a) to desorption (k_d) at equilibrium, is then obtained. The Langmuir constant, b, is a dimensionless quantity and can be calculated using the modified equation for the adsorption of macromolecules from the liquid phase [12], based on the usual gas phase adsorption [15]. The obtained b constant from the Langmuir plots at characteristic fragments of DGEBA is shown in Table 6. It is found that there is relative closeness in the b values from the fragments at $m/z = 77$, 91, 135, and 191 Da. The b value from the ion at $m/z = 57$ Da is much greater than that from the other ions. This may be because this ion is less characteristic of DGEBA as discussed above. So, $m/z = 57$ Da was disregarded for the calculation of the average b value. The calculation of the average of four values from the fragment at $m/z = 77$, 91, 135, and 191 Da is equal to 104.4. The standard deviation, σ, is 23.5. It should be noted that such a range is rather small, considering the various calculations involved the inevitable difference in ionisation cross section and the conventional belief that the ToF-SIMS technique cannot readily provide quantitative information.

No obvious fragment demonstrating the presence of a specific covalent bond was encountered in the spectra of DGEBA deposited on GPS-coated aluminium. Therefore, we assume that the strong specific interactions occurring between GPS and DGEBA are of a Lewis acid-base nature or via hydrogen bonding.

Moreover, the b values allow for the calculation of the fractional monolayer coverage, θ, by means of an Equation, $\theta = bC/(1 + bC)$. Surface coverage was plotted as a function of the solution concentration, as shown in Fig. 8. It is clearly seen that all curves reach a plateau line at the surface coverage θ of approximately 0.9. This value is close enough to 1 to consider that full coverage has been reached. It means that all aluminium sites are totally occupied by DGEBA molecules. This forms a complete monolayer. The sharpness of the 'knee' of the adsorption isotherm is known to provide a qualitative indication of the interaction energy, Q. It is gratifying to note that all the isotherms of Fig. 8, with the exception of that constructed from the data of $m/z = 57$ Da, have similar initial gradients. This provides further evidence of the reliability of the quantitative adsorption data provided by ToF-SIMS. The

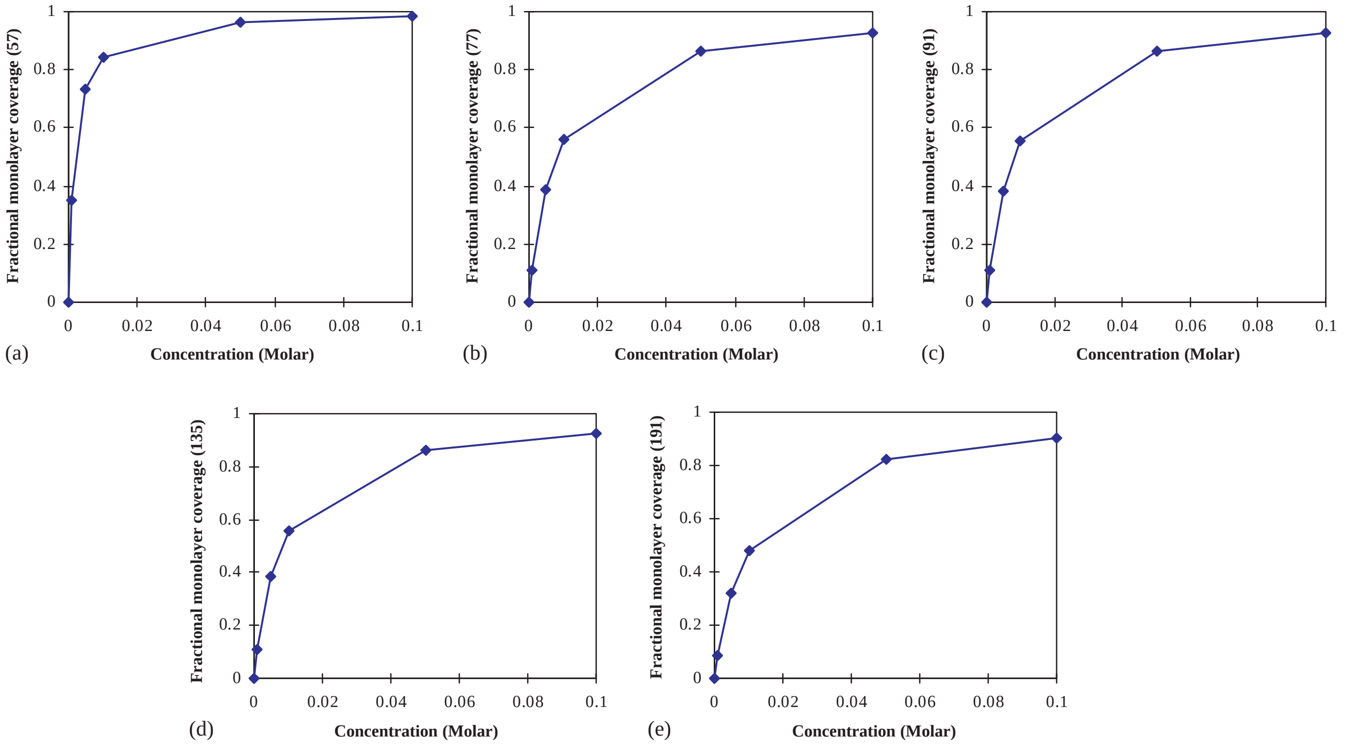


Fig. 8. Fractional monolayer coverage of the fragments at mass (a) 57, (b) 77, (c) 91, (d) 135, and (e) 191, using Langmuir equation.

inconsistency of the data from $m/z = 57\,\mathrm{Da}$ provides further evidence that this ion is not solely characteristic of the DGEBA adsorbate.

6. Conclusions

In this study, ToF-SIMS was employed to study the adsorption of uncrosslinked epoxy resin, DGEBA, onto GPS-coated aluminium in terms of the kinetics and the thermodynamics of the adsorption process.

In the case of the kinetic studies, it was found that a 10 min exposure time was the adequate time to reach an adsorption equilibrium. In the case of the thermodynamic studies, the treatment with $5 \times 10^{-2}\,\mathrm{M}$ of DGEBA solution provides the saturation uptake of DGEBA molecules onto the GPS-coated aluminium.

ToF-SIMS provides no evidence of the formation of a specific primary bond between DGEBA and either substrate. The level of adhesion observed is therefore attributed to Lewis acid–base interaction. The adsorption isotherm is of the Langmuir type, giving a better fit than a Temkin type. The Langmuir isotherm indicates that DGEBA adsorbed on a GPS-coated aluminium surface as a monolayer. The modified form of the Langmuir equation provides the rate constant b in order to construct the fractional monolayer coverage. It was found that the surface coverage of DGEBA on aluminium substrate is as a complete monolayer.

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