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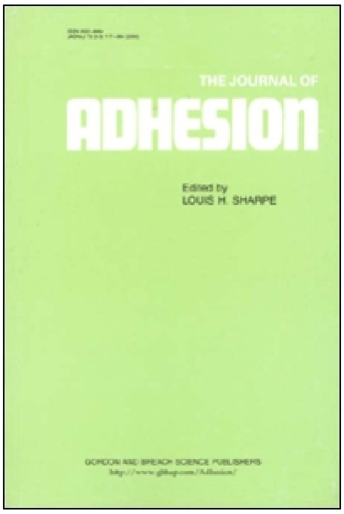

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P. M. Hobbs[a]; A. J. Kinloch[a]

[a] Department of Mechanical Engineering, Imperial College of Science, Technology and Medicine, London, UK

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The Computational Molecular Modelling of Organosilane Primers

P. M. HOBBS and A. J. KINLOCH*

Department of Mechanical Engineering, Imperial College of Science, Technology and Medicine, Exhibition Rd., London, SW7 2BX, UK

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The adhesion of a series of organosilanes, with varying lengths of alkyl chain, adsorbed on different metal-oxide substrates, have been modelled using a computational molecular dynamics (MD) approach. The silanes modelled were: (a) the fully-hydrolysed version of γ-glycidoxypropyltrimethoxysilane (GPMS), (b) the fully-hydrolysed version of γ-glycidoxydecyltrimethoxysilane (GDMS), and (c) the fully-hydrolysed version of γ-glycidoxyeicosyltrimethoxysilane (GEMS). The substrates were corundum (α-Al_2O_3), an amorphous form of aluminium oxide (amorphous alumina, Al_2O_3) and haematite (Fe_2O_3). We have modelled (a) the effect of varying the length of the alkyl chain, (b) the effect of the type of substrate and (c) the effect of water attacking the organosilane/metal-oxide interface. Wherever possible, the results from the MD simulations have been compared with results from experimental studies, and very good agreement has been found between the theoretical predictions and the experimental results.

Keywords: Amorphous alumina; computational modelling; corundum; durability; haematite; molecular dynamics; molecular modelling; organosilanes; self-assembling monolayers; effect of water; work of adhesion

1. INTRODUCTION

Organosilanes have been used for many years to improve the adhesion, and resistance to water attack, of polymer/metal and polymer/ceramic interfaces [1–3]. These organosilanes possess the general chemical formula R′-Si(R)$_3$, where R′ is usually a short carbon chain containing some additional chemical functionality capable of reacting with the polymeric coating or adhesive. The group R is a

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*Corresponding author.

hydrolysable end-group such as an ethoxy, methoxy or chloro group which can react with water present, either in the pretreatment solution or adsorbed on the surface of the substrate. This reaction forms silanol (Si—OH) groups. The enhanced adhesion that the organosilanes primers can offer, compared with conventional polymeric coatings and adhesives, is generally considered [2] to be due to the silanol groups strongly interacting, either physically or chemically, with the surface of the substrate.

More recently, experimental work has been performed by Cave and Kinloch [4] who synthesised and studied the adhesion of organosilanes with long alkyl chains, which were adsorbed on an aluminium-oxide substrate from solution. They found that, if the hydrocarbon chain (*i.e.*, the group R′) was greater than about eighteen carbon atoms in length, then the silane molecules would form a self-assembling monolayer structure. Such oriented monolayers were found to exhibit good adhesion, and impart good resistance to debonding of the interface in the presence of water.

Most recently, molecular dynamics simulations have been undertaken [5–7] to model the conformation of adsorbed silane primers, and the nature of their interactions with the substrate. Further, some initial attempts have been made to predict the tendency for water to displace the adsorbed organosilane layer. Clearly, if such computational modelling methods could be developed and verified, they would enable the more rapid development of novel, and more effective, silane primers.

Thus, a main aim of the present work is to use computational molecular modelling to study the adsorption of both short- and long-chained organosilane primers on different types of metal oxides. Of particular interest will be the verification of the predictions from the modelling, wherever possible, using the existing experimental data to be found in the literature.

2. COMPUTATIONAL MOLECULAR MODELLING

The present modelling studies are based upon using a molecular dynamics (MD) approach [5–9]. The MD technique uses what is essentially a mechanical model of the molecules under study. Atoms are represented as solid spheres with characteristic masses and radii.

Bonds, specific to the atom types they connect, are represented by springs with a nominal equilibrium (*i.e.*, zero applied force) length. Factors affecting molecular motion such as temperature, electrostatic charges and van der Waals' forces can be included in the dynamics calculations. The parameter set or "force field" (*i.e.*, atomic masses, bond lengths, bond angles, bond stretching energies, etc.) upon which the model is based may be ascertained from experimental data such as X-ray crystal structure determinations and vibrational spectra. The simulation of real-time molecular motion is undertaken by integrating Newton's laws of motion over time for the masses in the system after initial velocities have been imparted to them.

A molecular dynamics approach is based upon an energy minimisation process, and minimisation involves using a mathematical algorithm to locate the lowest energy conformation of a given structure. During a minimisation, the atomic co-ordinates of the molecules are adjusted in order to reduce the molecular energy. The energy of the system is calculated from a series of force-field terms that describe the interactions between the atoms. As noted above, the interactions include bond length terms, angle terms, torsion terms, non-bonded interactions and electrostatic charge terms. For each of these terms, the associated energy is defined by a suitable equation. For example, the bond length and angle terms are commonly expressed as harmonic potentials and the torsion term is based on the principle that some conformations are preferred over others.

Molecular dynamics (MD) is an adaptation of the minimisation process. A minimisation will take the molecule to the nearest lowest (local) energy conformation, but this does not necessarily represent the global minimum. In order to overcome this problem, a molecular dynamics calculation can be performed. In such a calculation, an initial velocity is placed on each of the atoms, which is related to a temperature factor. The atoms are allowed to move for a given time step, as governed by the force-field terms. Then, the energy of the new structure is calculated using the force-field terms, as in a minimisation calculation. As commented previously, the MD technique uses Newton's equations of motion to move the atoms in a system randomly in such a way as to generate new positions over a set time period. The movement of the atoms are constrained by the force field which is equivalent to that for molecular mechanics. The initial co-ordinates for the atoms are usually provided from the previous step, apart from the first step where they are provided from a knowledge of the starting structure. Initial velocities are assigned to the atoms at random from a Maxwell-Boltzmann distribution corresponding to the temperature, whilst the resulting accelerations are calculated from Newton's equations. After completing these calculations, the values of the co-ordinates, velocities and accelerations are updated: the old co-ordinates are replaced by the new ones; the velocities are deduced from the differences between the previous values and the new ones, divided by the time step (one femtosecond in the present work); and the accelerations are corrected by calculating the gradients, using the new values of the co-ordinates. This cycle is repeated many times during the course of the run, and the energy of the new structure of the system may be calculated each time using the force-field terms.

Thus, the basic idea of the MD approach is that by allowing the molecules under study to become "heated", they can overcome the energy barriers between localised minima, and allow a number of low energy positions to be observed. The structure after each time step is saved, allowing a trajectory file to be constructed which can subsequently be analysed. In the present work, we will run MD calculations on the various systems of interest; *i.e.*, on the various types of silanes adsorbed on the different types of metallic-oxide substrates, with and without the presence of water molecules. The lowest of the local minimum energy positions will be determined and, hence, (a) the preferred conformation of the adsorbed molecules and (b) the associated energies of their interfacial interactions will also be ascertained.

3. COMPUTATIONAL METHOD

3.1. Introduction

We have used the "Cerius^2" software package (Biosym/MSI, Cambridge, UK). The calculations were performed using the constant NVT method, where the number of atoms, N, volume, V, and thermodynamic temperature, T, are held constant. The time step employed was one femtosecond. The integration algorithm employed was the summed "Verlet" algorithm [10, 11].

The workstation employed for the studies was a Silicon Graphics Indy R4400 model and a typical MD simulation took from about two to three days for the lowest molecular-weight primers to about eight to ten days for the highest molecular-weight primers.

3.2. Force Field

The force field employed was the Dreiding II force-field [8, 12], as supplied with the Cerius^2 software package. Buckingham potentials were used for the non-bonding van der Waals terms, with the aluminium term being taken from the Burchard force-field [8], as devised by Bick [8, 13]. It should be noted that Buckingham potentials are a way of describing the van der Waals term in the force field; *i.e.*, they provide a definition of how the shape of the energy curve changes with interatomic distance. This is a weaker van der Waals term than that supplied for aluminium in the Dreiding II force field, as the stronger term caused the silane molecules to be repelled from the substrate surface. This approach can be justified, since the bonding at the surface would be weaker than within the substrate, and it is this bonding in which we are interested. The Ewald summation method was used for the non-bonding coulombic terms [8].

3.3. Metal-oxide Substrates and Organosilane Primers

3.3.1. The Substrates

Two common crystalline metal oxides were chosen for the substrates. These substrates were corundum (α-Al_2O_3) and haematite (Fe_2O_3), and were taken directly from the database in the Cerius^2 software package. The structural details for these metal oxides had been taken from previously-published work [8]. A third substrate was an amorphous form of aluminium oxide (amorphous alumina, Al_2O_3). This was of interest since many of the surface pretreatments used for aluminium alloys, prior to adhesive bonding or priming, lead to an amorphous oxide being produced on the surface of the treated alloy [2]. The amorphous form of aluminium oxide was built using the amorphous builder module in the Cerius^2 software package. Basically, this entailed building a single alumina molecule, which was then cloned a number of times. A unit cell was then filled to a density of 3.2 g/cm [14]. The resulting structure was then minimised to relax any interatomic distances which were too small. (If these are not relaxed, then the subsequent MD simulation may fail due to the very high repulsive energies associated with such unrealistic bond lengths). Formal charges were used for all three substrates; *i.e.*, −2e for oxygen, +3e for aluminium and +3e for iron.

3.3.2. The Organosilanes

The following organosilanes were employed in the current studies:

(a) The fully-hydrolysed version of γ-glycidoxypropyltrimethoxysilane (GPMS). This has a short alkyl chain length of three carbon atoms.
(b) The fully-hydrolysed version of γ-glycidoxydecyltrimethoxysilane (GDMS). This has an alkyl chain length of ten carbon atoms.
(c) The fully-hydrolysed version of γ-glycidoxyeicosyltrimethoxysilane (GEMS). This has a long alkyl chain length of twenty carbon atoms.

In these primers, therefore, all the methoxy groups on the silicon atom have been fully hydrolysed to give hydroxyl groups.

Structures for these primer molecules were built using the sketcher module in the Cerius^2 software package. A semi-empirical molecular orbital calculation (MOPAC) calculation [8] was then undertaken to calculate the electrostatic charges on the molecules. A unit cell was then built, and filled with a number of molecules until the density was equivalent to the experimental density. For example, for the GPMS primer, the experimentally-quoted [15] density is 1.07 g/cm^3 and we achieved a theoretical density of 1.07 g/cm^3. The silane molecules in the unit cell were then (a) minimised to relax any interatomic distances which were too small, (b) placed above the surface of the substrate, and (c) minimised again. Enough space was left above the primers in the unit cell so that they did not interact with the cell's periodic image in the adjacent unit cell overhead.

In the case of the hydrolysed version of γ-glycidoxypropyltrimethoxysilane (GPMS), one direct verification of the accuracy of the modelling of the silanes coule be readily undertaken. Namely, the solubility parameter, δ, of the GPMS primer could be deduced [16] from the MD simulation and was found to be 8.9 $(cal/cm^3)^{1/2}$. This value may be compared with the literature value [17] of 9.2 $(cal/cm^3)^{1/2}$; and the good agreement between the values gives strong support to the validity of the modelling work.

3.3.3. *Inclusion of Water Molecules*

For the calculations involving water molecules, the basic primer, substrate and primer/substrate systems were established in the same manner as that described above. The charges on the water molecules were taken from the literature [18] to be −0.82 e for oxygen and +0.41e for hydrogen. In the MD direct-simulation model (see below), the conformation of the primer was taken from the lowest energy structure from the MD run of the primers against the substrate. The water molecules were then introduced into the MD simulation.

3.4. Calculation Methods

Once a unit cell containing the substrate and primer had been built, a MD calculation was performed on the system. The atoms in the substrate were kept fixed during the simulation, and the primer molecules allowed to move. As stated previously, the MD modelling was undertaken using the constant NVT method. Calculations were performed for 1 ns, with a step size of 1 fs and with the structures being saved after every 100 steps. Periodic boundary conditions were applied to the unit cell [8]. (This allows the "contents" of the unit cell to be kept constant; *i.e.*, any molecules which exit the cell on one side reappear in the cell on the other side.) The MD simulation was run and the lowest energy structure for the system was extracted from the output, and the total energy of this system was then deduced *via* the software. The substrate was then removed from the simulation, and the energy of solely the primer molecules was now calculated. Since the fixed substrate obviously has no difference in energy before and after the MD simulation, the interfacial interaction energy is the difference between the total energy of the system and the energy of solely the primer molecules. The reproducibility of repeat computational runs for any given system was investigated and the conformations obtained were found to be very reproducible, with a scatter on the values of the interaction energies of typically ±5%.

For the substrate/primer, substrate/water and primer/water interfaces, the respective thermodynamic works of adhesion may be calculated from the value of the corresponding interfacial interaction energy, which is ascertained from the MD simulation, *via*:

$$\frac{\text{Interfacial interaction energy (J/mol)}}{\text{Surface area } (\text{m}^2) * \text{Avogadro's constant (1/mol)}} \tag{1}$$

Further, from the values of the thermodynamic work of adhesion for the various interfaces, we may also calculate the work of adhesion, W_{AL}, for the primer/substrate interface in the presence of water molecules, *via* the following equation [2, 19]:

$$W_{AL} = 2\gamma_w + W_A - W_{PW} - W_{SW} \tag{2}$$

where:

γ_w = surface free energy of water (taken to be 72.2 mJ/m^2)
W_A = work of adhesion of the primer/substrate interface
W_{PW} = work of adhesion of the primer/water interface
W_{SW} = work of adhesion of the substrate/water interface.

Now, calculation of the terms W_A and W_{AL} enables the environmental stability of the interface to be predicted. For example, the value of W_A, which corresponds to the primer/substrate interface in an inert atmosphere, is almost always found to be positive in value, and this indicates that such an interface is stable in a benign environment. However, in the presence of a liquid environment, such as water, the thermodynamic work of adhesion, W_{AL}, may have a negative value, indicating that the interface is now unstable and will have a thermodynamic tendency to dissociate. (Although the rate at which this occurs is governed, of course, by the kinetics of the process which, in turn, may be controlled by the rate of water diffusion, through the adhesive and primer, to the interface [2, 19]).

4. RESULTS AND DISCUSSION

4.1. Introduction

In the present work on the computational molecular modelling of silane primers, three main topics have been studied. These are:

(a) The effect of the carbon chain length in the series of organosilane primers adsorbed on the corundum (α-Al_2O_3) substrate.

(b) The effect of the substrate onto which the three organosilane primers (*i.e.*, the hydrolysed versions of GPMS, GDMS and GEMS) are adsorbed. The three different metal-oxide substrates studied were: (i) corundum (α-Al_2O_3), (ii) amorphous alumina (Al_2O_3), and (iii) haematite (Fe_2O_3).

(c) The effect of water on the stability of the interfaces of the three different organosilane primers (*i.e.*, the hydrolysed versions of GPMS, GDMS and GEMS) adsorbed on corundum (α-Al_2O_3). Also, in this aspect of the work, the stability in the presence of water of decane, polyethylene and a simple epoxy-containing monomer adsorbed on corundum (α-Al_2O_3) has also been studied for comparative purposes. (As for the silane primers, a semi-empirical molecular orbital calculation (MOPAC) calculation [8] was undertaken to calculate the electrostatic charges on these molecules).

In all cases the conformation of the adsorbed molecules have been modelled and quantitative information concerning (a) the nature and extent of the closest contacts between the adsorbate and the substrate, and (b) the interfacial interaction energy for the interface(s) has been obtained.

4.2. The Effect of the Carbon Chain Length

As discussed above, three organosilanes were chosen to examine the effect of varying the carbon chain length. To evaluate the effect of this chemical modification of the silane molecule on the interfacial chemistry, a unit cell with nine silane molecules was placed above a corundum surface and a MD simulation undertaken.

From Figures 1 to 3, several interesting observations may be noted. Firstly, the initial, starting, conformation used for the GPMS

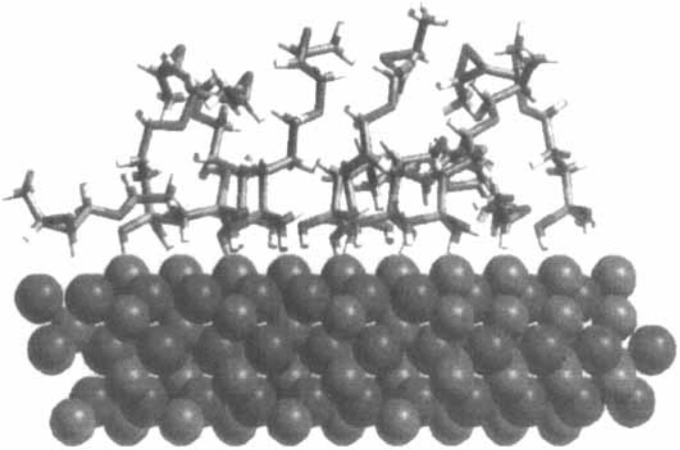

FIGURE 1 Molecular dynamics simulation of the fully-hydrolysed version of γ-glycidoxypropyltrimethoxysilane (GPMS) molecules adsorbed on corundum. (Grey: carbon; red: oxygen; pink: aluminium; white: hydrogen; yellow: silicon.) (See Color Plate IX).

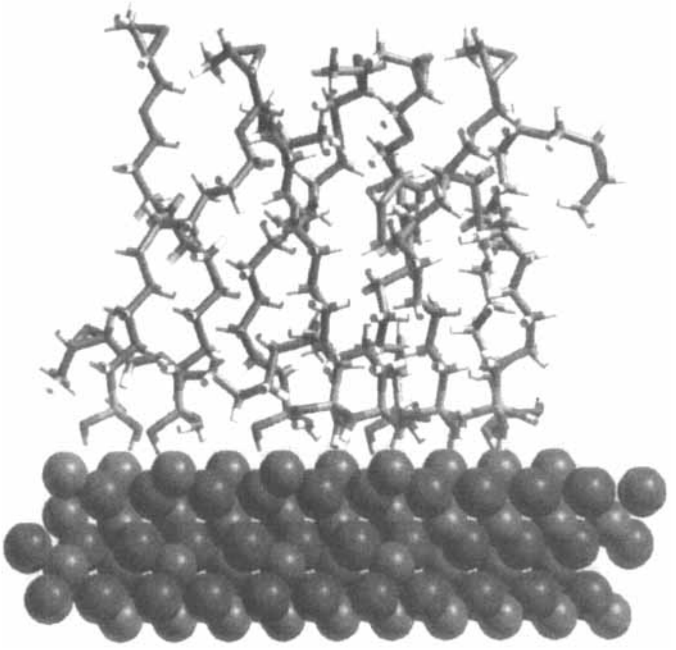

FIGURE 2 Molecular dynamics simulation of the fully-hydrolysed version of γ-glycidoxydecyltrimethoxysilane(GDMS)molecules adsorbed on corundum. (Grey: carbon; red: oxygen; pink: aluminium; white: hydrogen; yellow: silicon.) (See Color Plate X).

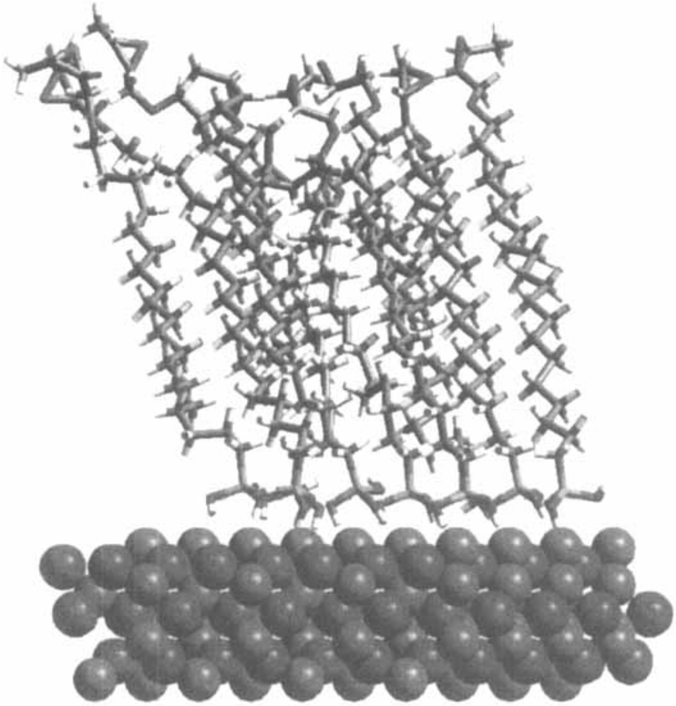

FIGURE 3 Molecular dynamics simulation of the fully-hydrolysed version of γ-glycidoxyeicosyltrimethoxysilane (GEMS) molecules adsorbed on corundum. (Grey: carbon; red: oxygen; pink: aluminium; white: hydrogen; yellow: silicon.) (See Color Plate XI).

molecules was with all the GPMS molecules vertical, with the hydroxyl groups on the silane end of the molecule pointing downwards towards the substrate surface. By the end of the MD run, a number of the molecules had fallen down, and were lying flat on the surface. Also, the molecules had disordered, compared with their starting positions and, indeed, were all pointing in different directions. These features are shown in Figure 1. Secondly, however, in the case of the silane which possessed the longer hydrocarbon chain length, *i.e.*, the GDMS, only one molecule had fallen down towards the surface. However, some of the other molecules were pointing in various directions. These features may be seen in Figure 2. Thirdly, in the case of the silane which possessed the longest hydrocarbon chain length, *i.e.*, the GEMS, at the end of the MD run the GEMS molecules had ordered themselves so that they were all at an inclination angle of approximately 52° to the surface, as may be seen in Figure 3.

The above results from the present modelling studies are summarized in Table I. The inclination angle is an average of all the values for the nine organosilane molecules adsorbed on the corundum surface and the scatter from the average value of the inclination angle is also quoted. Closest atomic contacts between the silane primer and metal-oxide surface are also given, and in all cases the shortest interfacial bonds were between the hydrogen atom in the hydroxyl group on the silane primer and the oxygen atom in the α-Al_2O_3 surface. Thus, in agreement with the experimental observations [1–3], it is the silanol end of the primer molecule which exhibits the strongest interactions with the metal-oxide surface.

The results shown in Table I are also in very good agreement with the previous experimental results of Cave and Kinloch [4]. For example, the work of these authors showed that the hydrocarbon chain length had to exceed about eighteen carbon atoms in order to obtain a self-assembling, and so a highly-ordered, silane layer. From the results shown in Table I, it may be seen that only the GEMS (with twenty carbon atoms in its hydrocarbon chain) gives a high degree of order, as revealed by the very low degree of scatter in the inclination angle. Further, the inclination angle measured by Cave and Kinloch [4] was about 60°, which is in good agreement with the values deduced from the present computational modelling studies.

4.3. Effect of Substrate

The effect of substrate was studied by modelling the adsorption of the three silanes (*i.e.*, the hydrolysed versions of the GPMS, GDMS and GEMS) on the three different types of oxides (*i.e.*, corundum (α-

TABLE I Inclination angles and average closest interfacial contacts for various organosilane/corundum interfaces

Primer	*Inclination angle*	*Closest contact*
GPMS	42° ± 23°	2.11Å ($H_{Silane}-O_{Surface}$)
GDMS	56° ± 36°	2.05Å ($H_{Silane}-O_{Surface}$)
GEMS	52° ± 4°	1.94Å ($H_{Silane}-O_{Surface}$)

Al_2O_3), amorphous alumina (Al_2O_3) and haematite (Fe_2O_3)). Again, a unit cell with nine silane molecules was placed above the metal-oxide surface of interest and a MD simulation undertaken. The results are shown in Table II and several noteworthy points emerge.

Firstly, for all the substrates, the degree of ordering of the GEMS primer molecules is far higher than for the other two primers (*i.e.*, the GDMS and GPMS primers) which possess shorter hydrocarbon chain lengths. This may be seen from the relatively low scatter in the value of the average angle of inclination of the GEMS to the substrate surface. As commented above, this is in complete agreement with the experimental work of Cave and Kinloch [4].

Secondly, for a given substrate, the values of the thermodynamic works of adhesion, W_A, are not greatly dependent upon the actual organosilane employed, although the value of W_A for the GEMS primer adsorbed on the amorphous alumina substrate does appear to be somewhat higher than the values of W_A for the other two silane primers adsorbed on this substrate. (It should be noted that the values of W_A were found not to be dependent upon the number of silane molecules used, when multiples of the unit cell were employed in the modelling studies).

Thirdly, for any given silane, the values of W_A with respect to the different substrates are in the ranking order of:

amorphous alumina (Al_2O_3) > corundum
(α-Al_2O_3) > haematite (Fe_2O_3)

TABLE II Thermodynamic work of adhesion, average contact angle and close contact for organosilanes adsorbed on corundum, amorphous alumina and haematite

Primer	*Corundum (α-Al_2O_3)*			*Amorphous alumina (Al_2O_3)*			*Haematite (Fe_2O_3)*		
	W_A	*I.A.*	*C.C.*	W_A	*I.A.*	*C.C.*	W_A	*I.A.*	*C.C.*
GPMS	940	42° ±23°	2.11 Å	1550	72° ±17°	1.96 Å	145	76° ±16°	2.53 Å
GDMS	870	56° ±36°	2.05 Å	1585	54° ±10°	1.50 Å	150	66° ±7°	2.47 Å
GEMS	785	52° ±4°	1.94 Å	1900	53° ±3°	1.86Å	145	63° ±2°	2.63 Å

W_A = Thermodynamic work of adhesion (mJ/m^2) (Scatter of about ± 5%).
I.A. = Inclination angle.
C.C. = Closest contact of the silane to the oxide surface.

This ranking is in agreement with previous work [5] where the adhesion of the hydrolysed GPMS was modelled, and the interaction of the GPMS with the amorphous alumina found to be significantly greater than for haematite. However, the present authors know of no experimental work on this subject. Hence, this prediction from the computational modelling must remain an interesting observation awaiting experimental evidence before any further comments may be offered.

Fourthly, the closest atomic contacts between the organosilane primer and the substrate are given in Table II, and in all cases the shortest interfacial bonds were between the hydrogen atom in the hydroxyl group on the silane primer and the oxygen atom in the metal oxide surface. This again confirms the relatively strong attraction of the silanol end of the primer molecules for the metal-oxide surface, as has been experimentally observed [1–3]. Also, as may be seen, the actual bond distance generally correlates with the value of W_A, the higher the value of W_A then the shorter the bond length for the closest contact. This is, of course, as would be expected.

4.4. Modelling the Attack by Water on the Silane/Metal-oxide Interface

4.4.1. Introduction

The stability of the primer/substrate interface is of major industrial interest. This is because a major reason for the use of the organosilane as primers is to increase the durability of adhesive joints or polymeric-coated substrates, where a metallic, or ceramic, material is the substrate.

In the present work, two approaches to modelling the attack by water on the silane/metal-oxide interface have been attemped. Firstly, the thermodynamic works of adhesion have been deduced from using Eq. (1) for each interface of interest in turn, and then these individually-deduced values have been combined *via* Eq. (2) in order to ascertain the value of W_{AL} for the primer/substrate interface whose durability is being examined. This initially appeared to be the most straightforward way of using the MD modelling in order to predict the stability of a given interface. Secondly, due to the problems encountered using this approach, as detailed below, we developed an alternative approach. This second method involves using the MD simulations to model directly a silane/metal-oxide interface in the presence of water molecules, and directly observing whether the water molecules do displace the silane molecules from the surface of the substrate. Also, the change in the interaction energy for any displacement of the adsorbate by the water molecules may be deduced, in order to quantify the results from this approach.

The primer/substrate interfaces examined consisted of the various organosilanes adsorbed on corundum. However, to aid interpretation of the results from these interfaces, we also examined the stability of a decane/corundum interface, a polyethylene/corundum interface and an epoxy/corundum interface.

4.4.2. Approach 1 – Via Calculation of the Individual Values of the Thermodynamic Works of Adhesion

Initially the MD simulations were undertaken on the following interfaces where the thermodynamic works of adhesion were calculated for these interfaces from the value of the corresponding interfacial interaction energies *via* Eq. (1):

(a) Hydrolysed GPMS on corundum – as before, a unit cell with nine silane molecules was placed above the corundum surface and a MD simulation undertaken.

(b) Polyethylene on corundum – here we built an idealised model of a polyethylene molecule, with about thirty carbon atoms along the chain. For the MD simulations we either employed one such molecule or four such molecules.

(c) Decane on corundum – a unit cell with nine decane molecules was placed above the corundum surface and a MD simulation undertaken.

The results for the values of the thermodynamic works of adhesion, W_A, in an inert atmosphere for these various interfaces are shown in Table III. As may be seen, the values of W_A are all positive in value, indicating that the various interfaces are stable, with no thermodynamic tendency to dissociate.

TABLE III Approach 1 – Calculation of the individual thermodynamic works of adhesion: Stability of adsorbate/corundum interfaces in the presence of water

Adsorbate	W_A (mJ/m^2)	W_{AL} (mJ/m^2)	**Interface stable in water?*
GPMS	940	35	Yes
Polyethylene (1 molecule)	380	−390	No
Polyethylene (4 molecules)	425	−385	No
Decane	360	−395	No

W_A = Thermodynamic work of adhesion.
W_{AL} = Thermodynamic work of adhesion in the presence of nine water molecules.
*Theoretical predictions concerning interfacial stability in the presence of water from the MD modelling studies are stated.

We next undertook a MD simulation of water molecules adsorbed on the corundum surface. Since the majority of the above modelling work has been undertaken using nine primer, or decane, molecules, the choice of nine water molecules to use in the MD simulations appeared to be self-evident. The value of W_{SW} for the corundum/water interface was $820\,mJ/m^2$. In a similar manner, the values of W_{PW} for the adsorbate/water interfaces were also deduced. Hence, with the various values of the thermodynamic works of adhesion now calculated, the thermodynamic works of adhesion, W_{AL}, of the various interfaces in the presence of water could be deduced *via* Eq. (2). These values are also given in Table III. As noted above, if in the presence of a liquid such as water the thermodynamic work of adhesion, W_{AL}, has a negative value, then this indicates that the interface is now unstable and will have a thermodynamic tendency to dissociate. As may be seen from Table III, only the value of W_{AL} for the GPMS/corundum interface is positive, which reveals that only this interface would be stable in the presence of water. This appeared to be an excellent prediction, since it is known [2] that this is indeed the only one of these interfaces which would not be significantly adversely affected by water.

However, the value of W_{SW} used in Eq. (2) for the corundum/water interface is clearly critical in these calculations and we, therefore, next considered the effect of the number of water molecules used in the MD modelling to obtain the value of W_{SW}. As is shown in Figure 4, the value of W_{SW} for the corundum/water interface is clearly very dependent upon the number of water molecules that is employed in the

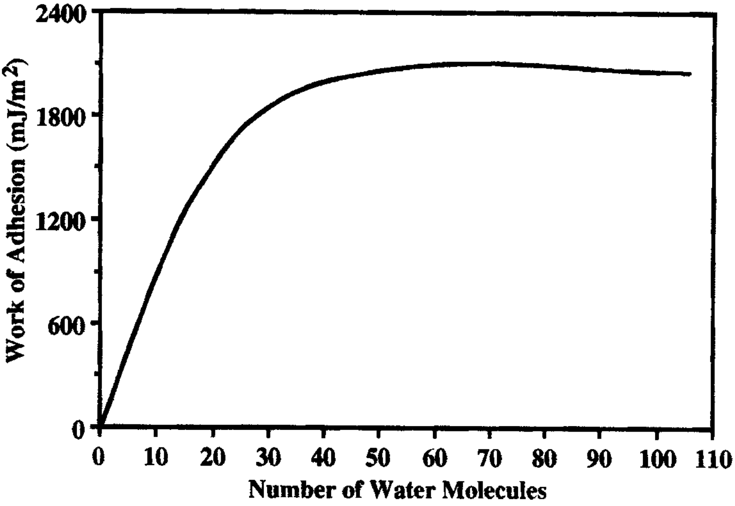

FIGURE 4 Work of adhesion, W_{SW}, deduced from a molecular dynamics simulation of the corundum/water interface *versus* the number of water molecules adsorbed.

MD model. Hence, the values that are derived *via* Eq. (2) for the thermodynamic works of adhesion, W_{AL}, of the various interfaces in the presence of water are very dependent upon the choice of the number of water molecules. As an example, in Table IV the values of W_{AL} which are obtained *via* Eq. (2) when either nine or fifty-two water

TABLE IV Approach 1 – Calculation of the individual thermodynamic works of adhesion: Stability of various interfaces in the presence of water – as a function of the number of water molecules assumed to be present

	9 water molecules		*52 water molecules*	
Adsorbate on corundum	W_{AL} *(mJ/m²)*	**Interface stable in water?*	W_{AL} *(mJ/m²)*	**Interface stable in water?*
GPMS	35	Yes	−1170	No
Polyethylene (1 molecule)	−390	No	−1595	No
Polyethylene (4 molecules)	−385	No	−1590	No
Decane	−395	No	−1600	No

W_{AL}= Thermodynamic work of adhesion in the presence of nine or fifty-two water molecules, as indicated in Table.

*Theoretical predictions concerning interfacial stability in the presence of water from the MD modelling studies are stated.

molecules are used to ascertain the value of W_{SW} for the corundum/water interface are given. (The choice of fifty-two water molecules was simply based upon the fact that this corresponds to the water molecules in the unit cell having a density of $1 \mathrm{g/cm^3}$). Clearly, the values of W_{AL} for the various interfaces in the presence of water are very dependent upon the number of water molecules employed in the MD model. Hence, the predictions of the stability of the interface are also very dependent upon the choice of the number of water molecules used in the MD model.

Further, as might be expected, similar trends to those illustrated in Figure 4 were found for the values of W_{PW} for the adsorbate/water interfaces, and this makes the calculations of the values of W_{AL} even more sensitive to the choice of the number of water molecules used in the MD simulations. Since we do not know the number of water molecules which will displace the adsorbate, and be attracted to the substrate surface, we developed a second, more direct, approach for modelling water attack on the primer/substrate interface.

4.4.3. Approach 2 – Via MD "Direct Simulation" of Water Attack

Basic Model In the second approach a system has been built which consists firstly of the substrate surface covered with a layer of adsorbate molecules (in the case of the organosilanes, nine molecules have been used). Secondly, a layer of water molecules has been added. Thirdly, an upper layer of "capping" adsorbate molecules has been added. In this layer the adsorbate molecules are fixed and simply act to restrict the water molecules so that they cannot completely escape from the system, *i.e.*, we have a "reservoir" of water molecules. This is illustrated in Figure 5 for the case of the GPMS primer. The number of water molecules in the reservoir may be varied and the number which diffuse down to the oxide surface and displace the silane, or whatever adsorbate is modelled, may be ascertained. Also, the change in the interaction energies between the start and finish of this MD simulation may be deduced. From this value, the thermodynamic work of adhesion, W_{AL}, of the interface in the presence of water cannot be deduced, since the individual values of the various thermodynamic works of adhesion are not known, of course.

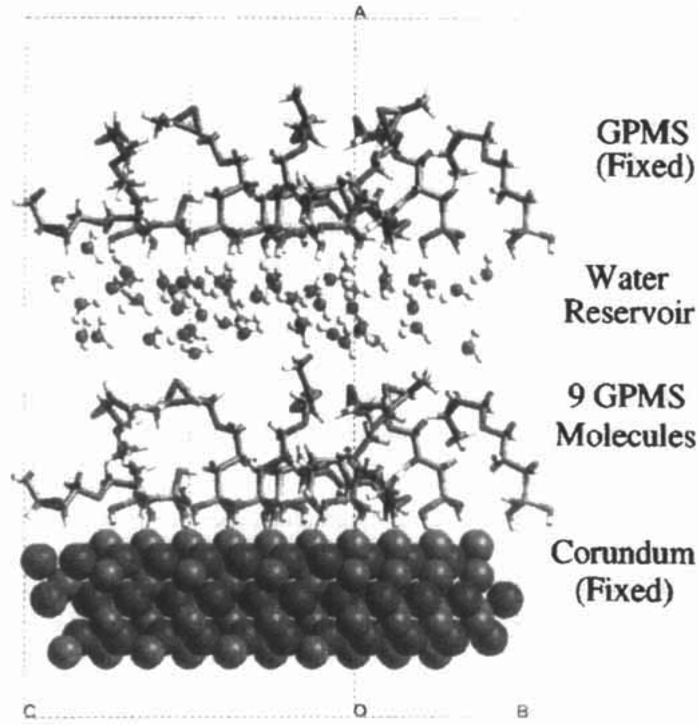

FIGURE 5 Molecular dynamics "direct-simultation" model for simulating the attack by water on the fully-hydrolysed GPMS/corundum interface, initial state (*i.e.*, time = zero). (Grey: carbon; red: oxygen; pink: aluminium; white: hydrogen; yellow: silicon). (See Color Plate XII).

However, the relative changes in the values of the interaction energies enables the ranking of the stability of the various interface in the presence of water molecules to be determined.

We need to consider the number of water molecule to place in the reservoir in the MD simulation the equilibrium solubility parameter for water in the silane is of the order [20] of 0.1% w/w and this leads to approximately one water molecule for every one hundred GPMS molecules. However, this system is too large to model using the current computing facilities. Also, if the one water molecule in the reservoir was preferentially attracted to the substrate, then another water molecule would, presumably, simply arrive *via* a diffusion process to the reservoir. Hence, we studied the effect of using various numbers of water molecules in the reservoir. The number was varied from nine to one hundred and four and the results are shown in Table V. As may be seen, for the GPMS/corundum system the number of water molecules which were attracted down to the surface of the substrate increased when the reservoir was increased from fifty-two water molecules, but no further increase was seen if one hundred and four water molecules were placed in the reservoir. Since the system with one hundred and four water molecules in the reservoir takes a very long time to run using the computing facilities available, further studies concentrated on using nine or fifty-two water molecules in the reservoir.

Ranking of Interface Stability in the Presence of Water The systems studied using our MD direct-simulation model were:

(a) Hydrolysed GPMS or GDMS or GEMS on corundum – as before, a unit cell with nine silane molecules was placed above the corundum surface and a MD simulation undertaken.
(b) Polyethylene on corundum – here we built an idealised model of a polyethylene molecule, with about thirty carbon atoms along the chain. For the MD simulations we employed four such molecules in the calculations.
(c) 1, 2 epoxypropyl-propyl ether on corundum – this was used to represent a simple epoxy-terminated monomer molecule, and a unit cell with nine such molecules was placed above the corundum surface and a MD simulation undertaken.

The initial number of water molecules which were placed in the reservoir and the final number of water molecules which diffused down to the surface of the substrate, effectively displacing the adsorbate, are

TABLE V Approach 2 – MD "direct-simulation" model: Initial number of water molecules used in the model and the final number attracted to the corundum surface – after 1000 dynamics steps for various adsorbates

Initial no. used in model	*Final number of water molecules attracted to adsorbate surface*				
	GPMS	*GDMS*	*GEMS*	*PE*	*Epoxy*
9	8	6	7	7	9
52	14	18	–	19	29
104	10	–	–	–	–

"–" means that the runs were not undertaken.

shown in Table V. In the case of the GPMS/corundum interface, the starting and final structures from the MD direct simulation are shown in Figures 5 and 6, respectively. As commented previously, the fact that some of the water molecules have been preferentially attracted to the surface of the corundum, and displaced the GPMS primer molecules, can be clearly seen. Further, it is of interest to note that the water molecules which were preferentially attracted to the surface of the corundum always tended to gather in clusters of two or three molecules, rather than be randomly distributed as isolated molecules.

In Table VI the change in the interaction energies between the start (*e.g.*, Fig. 5) and finish (*e.g.*, Fig. 6) of the MD direct-simulation model of water attack for the various systems are given. There are several noteworthy points.

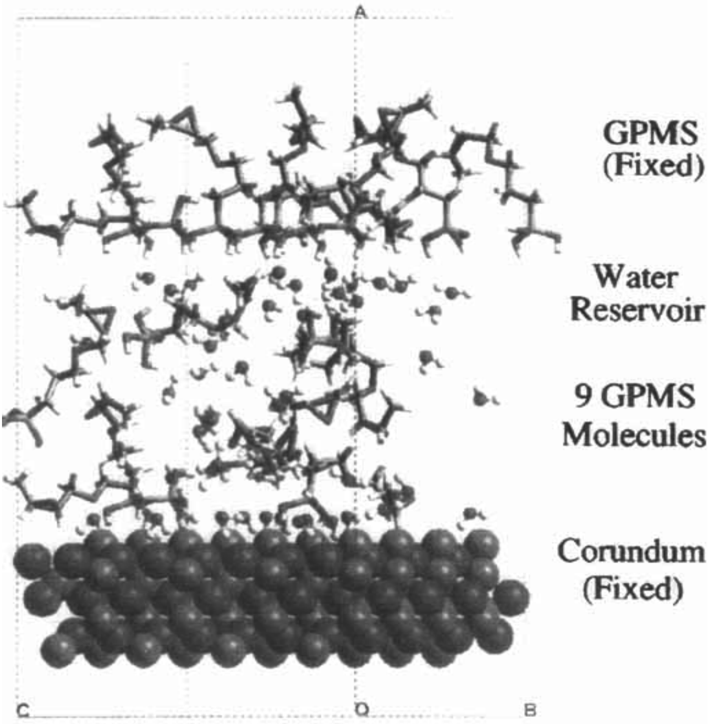

FIGURE 6 Molecular dynamics "direct-simulation" model for simulating the attack by water on the fully-hydrolysed GPMS/corundum interface, final state (*i.e.*, time = 1 ns). (Grey: carbon; red: oxygen; pink: aluminium; white: hydrogen; yellow: silicon). (See Color Plate XIII).

TABLE VI Approach 2 – MD "direct-simulation" model: Change in the interaction energy (kJ/mol) for adsorbate/corundum interfaces with nine or fifty-two water molecules present initially in the "reservoir"

Nine water molecules present, stability of interfaces in presence of water:

GEMS	>	GDMS	>	GPMS	>	Epoxy	>	PE
+3475	>	+1360	>	+560	>	+535	>	−1835

Fifty-two water molecules present, stability of interfaces in presence of water:

GDMS	>	GPMS	>	Epoxy	>	PE
+1020	>	+835	>	+210	>	−675

Firstly, as stated previously, the thermodynamic work of adhesion, W_{AL}, of the interface in the presence of water could not be deduced by this MD modelling approach. Thus, only a ranking of the predicted stability of the interface in the presence of water may be ascertained, and not a definitive criterion. (That is, the absolute values of the change in the interaction energies between the start and finish of the MD simulations are not a guide to whether the value of W_{AL} will be positive or negative and, hence, cannot be used to give an absolute statement as to the stability of the interface being modelled). Secondly, considering the ranking of the stability of the various interfaces, the modelling results predict that the GEMS/corundum interface will have the greatest stability in the presence of water, and that the polyethylene/corundum interface will be the least stable, since the former interface gives rise to the largest (positive) increase in the change of the interaction energy when the MD model with the water molecules is run, whilst the latter interface is associated with the largest (negative) decrease in the interaction energy. Thirdly, the ranking order is the same whether nine of fifty-two water molecules are in the reservoir. Hence, the ranking order is independent of the starting model, as it should be, of course. Finally, the ranking order is in complete agreement with the experimental results reported in the literature [2, 4]. For example, the three silanes adsorbed on corundum have a better stability in the presence of water than the epoxy monomer which, in turn, is more stable than the polyethylene adsorbate. Also, of the three silane primers, the longer the hydrocarbon chain length, then the greater the stability of the resulting silane-primer/corundum interface.

5. CONCLUSIONS

The adhesion of a series of organosilanes adsorbed on different metal-oxide substrates has been modelled using a computational molecular dynamics (MD) approach. The silanes modelled were: (a) the fully-hydrolysed version of γ-glycidoxypropyltrimethoxysilane (GPMS), (b) the fully-hydrolysed version of γ-glycidoxydecyltrimethoxysilane (GDMS), and (c) the fully-hydrolysed version of γ-glycidoxyeicosyltrimethoxysilane (GEMS). The substrates were corundum (α-Al_2O_3), an amorphous form of aluminium oxide (amorphous alumina, Al_2O_3) and haematite (Fe_2O_3).

Firstly, we have studied the effect of the alkyl chain length incorporated into the organometallic silane. The results were found to in very good agreement with the previous experimental results of Cave and Kinloch [4]. For example, the work of these authors showed that the hydrocarbon chain length had to exceed about eighteen carbon atoms in order to obtain a self-assembling, and so a highly-ordered, silane layer. From the theoretical modelling results it was found that only the GEMS (with twenty carbon atoms in its hydrocarbon chain) gives a high degree of order, as revealed by the very low degree of scatter in the inclination angle. Further, the inclination angle measured by Cave and Kinloch [4] was about 60°, which is in good agreement with the values deduced from the present computational modelling studies. Finally, the interfacial interactions between the —OH group on the silane and the substrate surface have also been successfully modelled.

Secondly, the effect of varying the type of metal-oxide substrate has been modelled. For a given substrate, the values of the thermodynamic works of adhesion, W_A, were not greatly dependent upon the actual organosilane employed. However, for any given silane, the values of W_A with respect to the different substrates were in the ranking order of:

$$\text{Amorphous alumina } (Al_2O_3) > \text{corundum } (\alpha\text{-}Al_2O_3) > \text{haematite } (Fe_2O_3)$$

This ranking is in agreement with previous work [5] where the adhesion of the hydrolysed GPMS was modelled and the interaction with the amorphous alumina found to be significantly greater than for haematite. However, the present authors know of no experimental work on this subject. Hence, this prediction from the computational modelling must remain an interesting observation, awaiting experimental evidence before any further comments may be offered. The closest atomic contacts between the organosilane primer and the substrate were deduced, and in all cases the shortest interfacial bonds were between the hydrogen atom in the hydroxyl group on the silane primer and the oxygen atom in the metal oxide surface. This relatively strong interaction between the silanol group on the primer and the substrate surface is in agreement with the experimental results [1 – 3]. The actual interfacial bond distance generally correlated with the value of W_A the higher the value of W_A the shorter the bond length for the closest contact. This is, of course, as would indeed be expected.

Thirdly, the effect of water on the stability of the organosilane/corundum interface has been considered. The initial approach was to deduce values of the thermodynamic works of adhesion, W_{AL}, of the various interfaces in the presence of water. However, the values of W_{AL} were found to be very dependent upon the choice of the number of water molecules used in the MD calculations. Thus, an alternative approach was adopted, which involved a MD direct simulation of the problem of water attack on a given adsorbate/substrate interface. In this model, the substrate surface was covered with a layer of adsorbed primer molecules and a layer of water molecules was then added. Next, an upper layer of capping adsorbate molecules were added. In this layer the adsorbate molecules are fixed, thus restricting the water molecules so that they cannot completely escape from the system, *i.e.*, we have a reservoir of water molecules. The number of water molecules in the reservoir was varied and the number which diffused down to the oxide surface and displaced the silane, or whatever adsorbate was modelled, were also ascertained. Also, the change in the interaction energies between the start and finish of the MD direct-simulation model for water attack was deduced. (Although, from this value, the thermodynamic work of adhesion, W_{AL}, of the interface in the presence of water cannot be deduced, since the individual values of the various thermodynamics work of adhesion are not known). However, the changes in the values of the interaction energies did enable a ranking of the stability of the various interfaces in the presence of water molecules to be determined. The rankings predicted from this MD model were found to be independent of the number of water molecules placed in the reservoir, and were in excellent agreement with experimental observations.

Thus, we have developed, and verified, MD simulations of the adhesion acting across various organosilane/metal-oxide interfaces. We now aim to employ these MD computational models to predict the adhesion characteristics of different types of novel organosilane primers, continuing to verify, wherever possible, the results from the modelling studies by comparison with experimental results. It is hoped that such computational modelling methods will enable the more rapid development of novel, and more effective, organometallic primers.

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