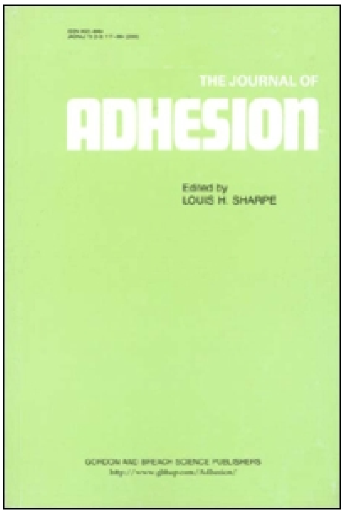

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Investigation of the Interaction of Silane-based Adhesive Primers with Metal Oxide Surfaces Using Molecular Dynamics Simulations*

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The interaction of organo-silane adhesive primers with metal oxide surfaces is investigated using molecular dynamics simulations. The organo-silanes studied are of the type used in commercial primers for epoxy adhesives. Aluminum oxide (amorphous) and iron oxide (hematite) are the metal oxide surfaces considered. The simulations are used to elucidate the effects of primer structure, metal oxide composition, morphology and level of hydration on fundamental aspects of the primer-surface interaction. Correlations are made between the results of simulations and previous experiments. The modeling approach may be useful in the design of improved adhesive bonding systems.

KEY WORDS Theory; molecular dynamics simulations; iron oxide; aminophenyl trimethoxy silane isomers; morphology; gamma-glycidoxypropyl trimethoxy silane; aluminium oxide; adhesion.

INTRODUCTION

Molecular dynamics (MD) simulations have recently been used to study the interaction between epoxy adhesive monomers and metal oxide surfaces.[1] These studies showed that the results of the simulations could be correlated to experimental observations of catalytic epoxy homopolymerization. In an extension of this work, molecular dynamics techniques are being used to investigate the interaction between organo-silane molecules (of the type used commercially as surface primers for adhesive bonding) and metal oxide surfaces. Some of the primer molecules under study have been the objects of previous experimental work while others are model

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compounds used to investigate various aspects of primer-surface interaction. Previously-studied primer molecules include γ-glycidoxypropyl trimethoxy silane (GPMS) and isomers of aminophenyl trimethoxy silane (n-APhMS; $n = 2, 3, 4$).[2,3] The surfaces being studied are amorphous alumina and hematite (a principal constituent of the surface of mild steels[4]). The principal models of the oxide surfaces use a fully ionic representation of the compounds (*i.e.* Al^{+3} and O^{-2}). Recently-published experimental and theoretical studies of the charge distribution on the alumina surface suggest that this representation is not accurate, and that the aluminum-oxygen bond has significant covalent character.[5,6] Nevertheless, the fully ionic representation has been used with some success in the previous study of interactions of adhesives with alumina.[1] Preliminary simulations utilizing a more sophisticated model[7] of the charge distribution in alumina and hematite have been carried out and are reported here.

EXPERIMENTAL

The molecular dynamics technique utilizes 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 (zero applied force) length. Factors affecting molecular motion such as temperature, electrostatic charges, and Van der Waal's forces can be included in the dynamics calculations. The parameter set or "force field" (atomic masses, bond lengths, bond angles, bond stretching energies, etc.) upon which the model is based is derived from experimental data such as x-ray crystal structure determinations and vibrational spectra. The simulation of real-time molecular motion is carried out by integrating Newton's laws of motion over time for the masses in the system after initial velocity is imparted to them (typically by using a random number algorithm). The principal limitation of the MD technique is that it is computationally intensive, since the time step over which integration is performed must be very small (on the order of one femtosecond (fs)) in order to avoid unrealistically large molecular motions. The length of simulated events is typically restricted to nanoseconds using the fastest computers currently available. Given the rapid advances being made in computer performance it is likely that the utility of the MD method and the number of reported applications of it will continue to grow.

Molecular dynamics simulations were carried out on a 12-node cluster of Silicon Graphics Indigo R4000 computers. The molecular dynamics algorithm is part of the molecular modeling program Sybyl[8] and the Tripos force field supplied with the program was used. Simulations were typically carried out for 50 picoseconds simulated time which required 10–15 hours computation time for a system with approximately 1500 atoms. Simulations were isothermal at 300 K and a time step of 1 fs was used. Structures for corundum and hematite were obtained from the crystallographic literature, the model of amorphous alumina was created as previously described.[1] Partial atomic charges and starting geometries of probe molecules (*i.e.* primers, water) were determined using the program MOPAC 5.0 as implemented in

Sybyl.[9] Published values of crystal ionic radii were used in the model metal oxide surfaces.[10]

INTERACTION OF γ GLYCIDOXYPROPYL TRIMETHOXY SILANE (GPMS) WITH ALUMINA AND HEMATITE

It is widely accepted by adhesive technologists that organo-silane primers such as GPMS enhance the durability of epoxy adhesive bonds to steel more effectively than for bonds to aluminum. A series of dynamics simulations has been carried out in an attempt to elucidate the causes of these observations. In these simulations a fully-hydrolyzed version of GPMS is used (*i.e.* $RSi(OH)_3$) which is believed to represent accurately the state of the primer molecule in actual adhesive applications.[2]

The structures resulting from dynamics simulations can be examined in several ways. The simplest of these is visualization which shows immediately the preferred orientation of the primer molecules on the oxide surface. More quantitative evaluation of the results may be obtained by computing the binding or interaction energy between the organic molecules and the surface, or by performing a structural analysis of the organic molecules which shows how critical bond lengths and angles are affected by their proximity to the oxide surface.

In the case of GPMS on amorphous alumina, visualization of structures from MD simulations shows that both ends of the GPMS molecule move rapidly into close contact with the oxide surface and remain there for the duration of the simulation. In the case of hematite, the epoxy functionality of the GPMS molecule is slower to reach the surface, while the silicon-bearing end interacts rapidly with the surface. Figure 1 shows snapshots of the two systems after about 30 ps of simulated time. The epoxy ends of GPMS are clearly far from the surface of hematite at this stage of the simulation, while they are interacting closely with alumina.

In preliminary simulations conducted using models of the surface with less than full charge separation, the effect is even more pronounced; over 90 ps of simulated time is required for epoxy groups to establish an interaction with the hematite surface. This behavior may contribute to the observation that GPMS is less effective as a primer for epoxy adhesives on aluminum than it is on steel. If both ends of the GPMS molecule are tightly bound to the alumina surface, then the functional groups of the first GPMS layer adsorbed may not be available for reaction with subsequently-deposited primer and/or adhesive. Such a condition could result in the formation of a weak boundary layer in the interphase region nearest the metal oxide surface.

Overall, GPMS binds more tightly to alumina than to hematite with calculated relative binding energies of -418 and -305 kJ, respectively. Analysis of GPMS bond lengths, particularly the carbon-oxygen bonds in the epoxy functionality, is not very conclusive, however, and shows only a small difference between the effects of alumina *vs.* hematite on this critical bond (Table I). One might expect that *if* the glycidyl group were indeed interacting more effectively with alumina than with hematite, the C—O bond length would be significantly more perturbed when approaching alumina. Silicon-oxygen bond lengths in GPMS do show a significant

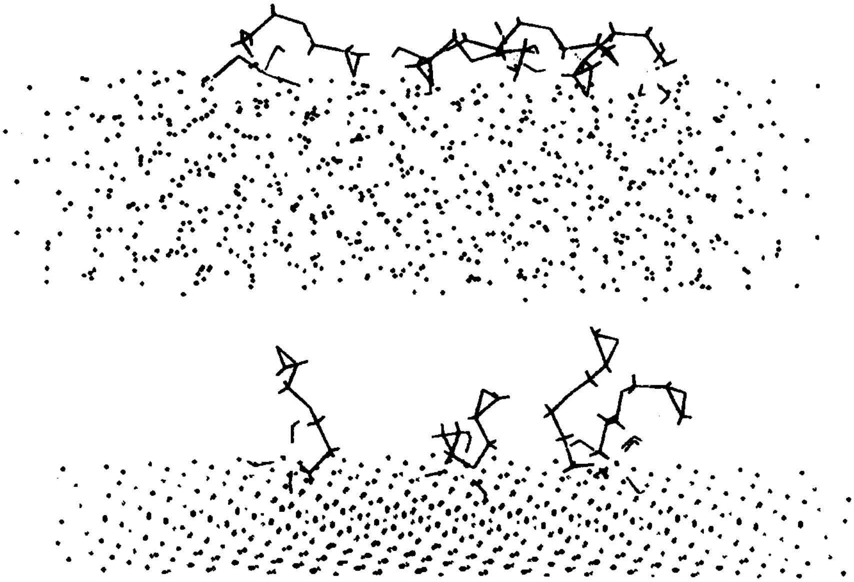

FIGURE 1 GPMS on metal oxide surfaces: Top, Amorphous Al_2O_3; Bottom, α-Fe_2O_3. Structures after 30 ps of molecular dynamics simulation. There are four molecules of GPMS on each surface. In GPMS, red = O; green = Si. In Al_2O_3, red = O^{-2}, blue = Al^{+3}. In α-Fe_2O_3, red = O^{-2}, yellow = Fe^{+3}. See Color Plate I.

variation in degree of perturbation on the two surfaces, which again points to a significantly stronger interaction of GPMS with alumina than with hematite.

INTERACTION OF MODEL VARIANTS OF γ-GLYCIDOXYPROPYL TRIMETHOXY SILANE (GPMS) WITH ALUMINA

Because the key site of interaction of GPMS with the oxide surfaces appears to be the silicon-bearing end of the molecule, simulations have been carried out to explore further the nature of the silane- (or siloxane-) surface interaction. One question to be answered is: how many of the Si—O functionalities can effectively interact with the surface at one time? In order to answer this question, model variants of the hydrolyzed GPMS molecule have been created in which one, two or three of the hydroxyl groups attached to silicon are replaced with methyl groups. These variants

TABLE I
Percent Increase in Median Bond Lengths in GPMS due to Interaction with Metal Oxide Surfaces

Bond	Amorphous Al_2O_3	Hematite
Si—O	20	14
C—O (epoxy)	2	0

are designated GPMS-X1, GPMS-X2 and GPMS-X3, respectively. Comparing the binding energies of the three molecules with amorphous alumina (Table II) it is clear that the critical number of Si—O sites for binding to the surface is two. Below this value, the binding energy decreases sharply.

In order to quantify the relative contribution of each of the functionalized ends of the GPMS molecule to the calculated surface affinity, a version of GPMS with an aliphatic group replacing the epoxy functionality has been simulated (C_8H_{17}—$Si(OH)_3$). This version of GPMS with the epoxy group removed has a calculated affinity for amorphous alumina of −326 kJ. The trimethyl silane version (GPMS-X3), however, has an affinity approximately one-third that of unmodified GPMS (−142 kJ, Table II). This observation supports the idea that the primary interaction of GPMS with the alumina surface is occurring through the siloxane end of the molecule with the ratio of the relative contribution of the silane and epoxy groups being greater than 2:1.

Simulations have been performed with the objective of determining what modifications to the GPMS structure might interfere with the apparent simultaneous interaction of the epoxy and siloxane ends of the molecule with alumina surfaces and reduce the calculated affinity of GPMS for alumina. The structures examined are γ-glycidoxy-α,β-diisopropyl-propyl trimethoxy silane (denoted Mod-1) and γ-glycidoxy, γ-*n*-nonylpropyl trimethoxy silane (denoted Mod-2) (Figures 2 and 3). The intent in simulating these model molecules was to devise a structure with significant steric hindrance so that both reactive groups of the primer molecule would not simultaneously interact with a metal oxide surface. These modifications succeeded in creating molecules with lower overall calculated affinities for the surface of alumina (Table III). The simulations do not, however, reveal any significant tendency for the modified molecules to interact with the surface only through the siloxane functionality as desired. Based on these results, it is not likely that compounds with the structures of GPMS Mod-1 or GPMS Mod-2 would display enhanced performance as adhesive primers on aluminum relative to GPMS.

TABLE II
Calculated Binding Energies of GPMS Variants with Reduced Siloxane Binding Sites to Amorphous Alumina (kJ)

GPMS	GPMS-X1	GPMS-X2	GPMS-X3
−418	−435	−293	−142

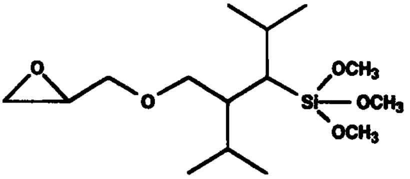

FIGURE 2 Structure of GPMS, Mod-1.

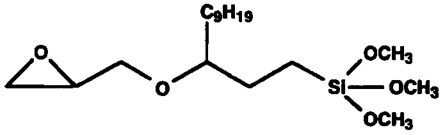

FIGURE 3 Structure of GPMS, Mod-2.

TABLE III
Calculated Binding Energies of GPMS Variants with Alkyl Side Chains to Amorphous Alumina (kJ)

GPMS	GPMS Mod-1	GPMS Mod-2
−418	−268	−197

INTERACTION OF AMINOPHENYL TRIMETHOXY SILANE ISOMERS (n-APhMS) WITH AMORPHOUS ALUMINA

Two aspects of the interaction of the APhMS molecules with oxide surfaces have been studied to date. One is the effect of structural isomerism on the ability of the primer to interact with the surfaces. The other is the role of the phenyl ring in the binding of the primer to the surface.

In practice, it is common to have a mixture of isomers present when using a primer based on a molecule such as APhMS. It is desirable to study each structure individually in order to determine which might be the most effective in binding to the surface. Such isolation is easily accomplished in the model environment and is one of the benefits of performing computational model studies. By performing dynamics simulations of pure 2-, 3- and 4-APhMS on amorphous alumina, one can gain insight into the unique aspects of each molecule's relationship with the surface.

Binding energy calculations (Table IV) show a trend toward more effective interaction as the substituents on the phenyl ring are moved further apart. This contradicts the intuitive expectation that the strongest binding could be obtained with the groups in the 2-position where the non-polar phenyl ring could remain relatively distant from the surface while the functional groups interacted with the surface. It is also intuitive, however, that the 4-substituted structure would have the best chance of simultaneously interacting with the surface and other components of the interphase as intended and, thus, would be the best primer. As with GPMS, it might be

TABLE IV
Calculated Binding Energies of *n*-APhMS/ACHMS to Amorphous Alumina (kJ)

	$n=2$	$n=3$	$n=4$
n-APhMS	−502	−565	−607
n-ACHMS	−435	−435	−435

expected that simultaneous effective binding of both primer functional groups to the surface would reduce the effectiveness of the primer on aluminum. All forms of APhMS show a tendency in simulations to interact with alumina surfaces through siloxane and amino groups simultaneously. In simulations it appears that the phenyl ring is forced into increasingly intimate contact with the surface as the functional groups are moved apart (Fig. 4), raising the question of whether the pi-electron system on the phenyl ring may be capable of making a significant positive contribution to the surface interaction energy.

To test this idea, a series of model molecules has been simulated in which the phenyl ring of *n*-APhMS is exchanged for a cyclohexyl ring. These molecules are designated *n*-ACHMS. Binding energy calculations do show somewhat reduced levels of attraction to alumina for the ACHMS series of molecules relative to APhMS (Table IV). It is also worth noting that the ACHMS binding energies are insensitive to the position of the silane and amine substituents on the ring. These results suggest that the phenyl ring may indeed be making a positive contribution to the surface interaction. This contribution may be even larger than the calculated affinity values suggest, in that some of the positive contribution of the phenyl ring to the binding energy of 4-APhMS will be offset by the accompanying induced strain energy (due to out-of-plane deformation of the phenyl ring near the alumina surface) which is not a factor with the flexible cyclohexyl structure. Thus, the phenyl structure is predicted to be ineffective in inducing what would appear to be a desirable

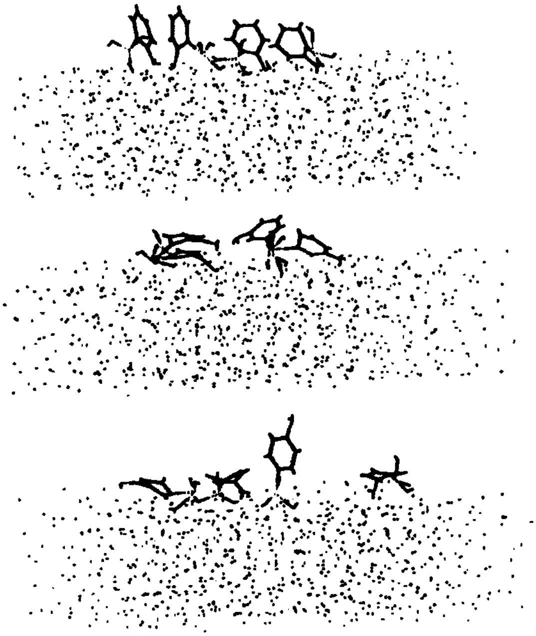

FIGURE 4 *n*-APhMS on amorphous Al_2O_3. Top to Bottom, $n = 2, 3, 4$. Structures after 50 ps of molecules dynamics simulation. There are four molecules of *n*-APhMS in each case. In APhMS, red = O; green = Si; violet = N. In Al_2O_3, red = O^{-2}, blue = Al^{+3}. See Color Plate II.

TABLE V
Effect of Adsorbed Water on Primer and Adhesive Binding Energies to Amorphous Alumina (kJ)

	Al_2O_3	Al_2O_3-wet	% change
GPMS	−418	−322	23%
2-APhMS	−502	−356	29%
DGEBA	−100	− 59	41%

orientation of primer molecules, that is, with only one functional group interacting with the metal oxide surface.

THE EFFECT OF WATER ON THE ADSORPTION OF SILANE PRIMERS ON METAL OXIDE SURFACES

The effect of water on the adsorption of primer and adhesive molecules on alumina has been simulated using an amorphous alumina surface with a previously-adsorbed layer of molecular water equivalent to 10% by weight of the alumina. The results, shown in Table V, indicate that the silanes are less affected by the presence of water than is the epoxy monomer, diglycidyl ether of bisphenol A (DGEBA). This result is in keeping with the observation that the use of silane primers improves the hydrolytic ageing properties of epoxy adhesive joints.

A set of preliminary simulations have been performed to probe further the influence of water on the interaction of the silane primers with metal oxide surfaces. In these simulations, a large amount (1000 molecules) of water is added to a system of 4 GPMS molecules interacting with a metal oxide surface at equilibrium. The resulting effect on the primer-surface interaction is then calculated. These preliminary results show that, in the case of alumina, the addition of water interferes with the interaction of the GPMS with the surface, in keeping with the calculated results of adding the primers to an already-hydrated surface. In the case of hematite, however, the primer-surface interaction appears to be enhanced (initial calculations show as much as 30% enhancement of GPMS binding energy). The primary difference between the interaction of water with alumina and hematite appears to be that water is capable of being accommodated within the hematite lattice at a smaller scale than within the amorphous alumina structure. Thus, water tends to be localized on the surface of small simulated fragments of alumina (*i.e.* 9 nm^3) while the simulation shows it to be largely absorbed into hematite fragments of similar size. It may be that this ability to accommodate water interstitially reduces the driving force for displacement by water of the adsorbed primer from the hematite surface.

CONCLUSIONS

Molecular dynamics simulations have been used to examine the interaction of organo-silane adhesive primers with metal oxide surfaces. The results of the simulations suggest the underlying causes of experimentally-observed differences in the environmental durability of epoxy adhesive bonds to aluminum and steel surfaces treated with such primers. The model suggests that in the case of primers having multiple reactive functional groups, the high polarity of the alumina surface (relative to that of hematite) binds all primer functional groups to the surface and inhibits the formation of a continuous, covalently-bonded pathway from the oxide surface to the bulk adhesive. The simulations illustrate how non-reactive components of the primer structure (phenyl rings, alkyl side chains) may influence the primer-surface interaction. A preliminary result has also suggested a mechanism in which the morphology of the metal oxide on the surface of a bonded metal substrate plays a critical role in the hydrolytic stability of adhesive bonds. Further experiments and simulations are needed to test these hypotheses. If the hypotheses prove correct, this modeling approach could be used in the design of interphase systems for adhesive bonding with improved environmental durability.

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