Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*)

REPORT DOCUMENTATION PAGE	**READ INSTRUCTIONS BEFORE COMPLETING FORM**
1. REPORT NUMBER 1st Interim 2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER –
4. TITLE (*and Subtitle*) The Molecular Modelling of Silane Primes for Adhesive Joints and Composite Materials	5. TYPE OF REPORT & PERIOD COVERED 1st Interim - Nov. 1995 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) A J Kinloch P M Hobbs	8. CONTRACT OR GRANT NUMBER(s) R&D 7736-MS-01 N68171-95-C-9118
9. PERFORMING ORGANIZATION NAME AND ADDRESS Mechanical Engineering Department Imperial College, Exhibition Road London SW7 2BX	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS United States Army European Research Office	12. REPORT DATE 29th November 1995 13. NUMBER OF PAGES 4
14. MONITORING AGENCY NAME & ADDRESS(*if different from Controlling Office*)	15. SECURITY CLASS. (*of this report*) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (*of this Report*) DISTRIBUTION STATEMENT A Approved for public release; Distribution Unlimited	
17. DISTRIBUTION STATEMENT (*of the abstract entered in Block 20, if different from Report*)	
18. SUPPLEMENTARY NOTES	
19. KEY WORDS (*Continue on reverse side if necessary and identify by block number*) Molecular, Modelling, Silane, Minimisation, Molecular Dynamics, Sorption, Adhesive Joints.	
20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*) The main aim of this work is to improve the understanding of the Molecular-level mechanism of adhesion of organosilanes on metal surfaces for the design of improved adhesion promoters/primers. Our approach will be to carry out molecular simulations to determine binding energies of the various molecular structures and the influence of surface contaminants, on the interaction of organosilanes with metal oxides. We will be using a variety of computer simulation methods incorporated in the Cerius^2 software.	

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The Molecular Modelling of Silane Primers for Adhesive Joints and Composite Materials

1. Introduction

Recently, experimental work has been performed in the Department of Mechanical Engineering at Imperial College of Science, Technology and Medicine by N.G. Cave and A.J. Kinloch(1) investigating the use of self-assembling monolayer silane films as adhesion promoters. This was followed up by computational work of M.S. Sennett(2) et al. and S.A. Ojo(3), examining the interaction of hydrolysed γ-glcidoxypropyltrimethoxysilane (GPMS) and nine variants thereof, on four metal oxide surfaces. We intend to continue on from this work, and initially attempt to use computer modelling methods developed in references two and three to reproduce the experimental results in reference one.

2. Aims

The main aim of this work is to improve the understanding of the molecular-level mechanism of adhesion of organosilanes on metal surfaces for the design of improved adhesion promoters/primers. Our approach will be to carry out molecular simulations to determine binding energies of the various molecular structures, and the influence of surface contaminants, on the interaction of organosilanes with metal oxides. We will be using a variety of computer simulation methods incorporated in the Cerius^2 software package(4), which are discussed below. We will correlate the models with experimental data in order to validate the model.

3. Computer Simulation Methods

3.1 Minimisation

Minimisation involves a mathematical algorithm to find the lowest energy of a given structure. During a minimisation, the atomic co-ordinates 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. The interactions include bond terms, angle terms, torsion terms, non-bonded interactions, and charge terms. In our calculations, the metal oxide surface will remain fixed. Initially we intend to take our silane molecules, and minimise them onto the surface, then examine the interactions.

3.2 Molecular Dynamics (MD) Calculations

Molecular Dynamics is an adaptation of the minimisation process. A minimisation will take the molecule to the nearest lowest energy, which is not necessarily the global minimum. In order to overcome this, a molecular dynamics calculation can be performed. This places an initial velocity on each of the atoms, which is related to a temperature factor. The atoms are allowed to move for a given time step, within the limits allowed by the force field terms, then the energy of the new structure is calculated using the force field terms, as in a minimisation calculation. By allowing the structure to be 'heated', it can overcome the energy barriers between localised minimum, 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 saved, which can be analysed at a later time. It is intended to run molecular dynamics calculations on the various molecules, to determine minimum energy positions and likely conformations and interactions.

3.3 Sorption and Minimisation

The sorption process allows molecules to be placed at random orientations above the metal oxide surface. An algorithm selects one of four methods to generate new positions :-

- Creation of a new position, according to a collision check, then an energy selection criteria based on probability.
- Destruction of a molecule - a molecule is removed according to the same energy/probability criteria as before.
- Rotation of an existing molecule by a random amount within a pre-defined limit.
- Translation of an existing molecule, again by a random amount within a pre-defined limit.

The energy is calculated for each molecule, and the position recorded, as in the previous dynamics calculations. This method allows us to build up a picture of many molecules on a surface, and how they are likely to pack together. It can also be used to generate up starting position for dynamics runs. Analysis of the results will allow us to build up a map of how the interaction energy changes with distance from the surface.

4. Conclusions

Initial work has concentrated on modelling basic straight chain alcohols from propan-1-ol to dodecan-1-ol. This is to enable the validation of a force field developed by Andreas Bick at Biosym/MSI(5), with respect to the hydrogen bonding that is expected. Once this has been validated, we will proceed on to examine the silanes. Once we have validated the force field against experimental values, we will then increase the complexity of our calculations to include water molecules. Once successful, we will then go on to develop suggestions of new, improved primer types, based on our findings.

5. References

[1] N.G Cave and A.J. Kinloch, *Polymer*, <u>1992</u>, **32**, 1162-1170.

[2] M.S. Sennet, S.E. Wentworth and A.J. Kinloch, *J. Adhesion*, <u>1995</u>, to be published.

[3] S.A. Ojo, M.Sc. Thesis, September 1995.

[4] Cerius^2 Molecular Modelling Software by Biosym/MSI, Cambridge, U.K.

[5] Personal communication with Andreas Bick, Biosym/MSI, Cambridge, UK.