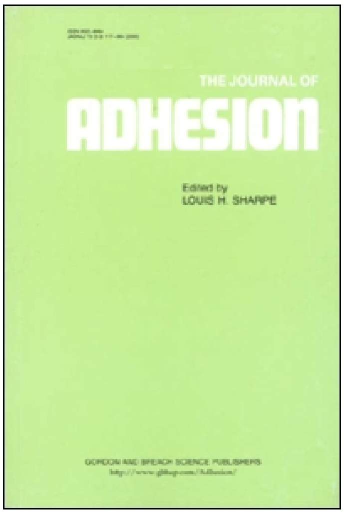

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Predicting the Work of Adhesion Using Molecular Modelling

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A combination of molecular modelling and thermodynamic techniques are employed to investigate the work of adhesion between materials, in particular to predict the probable stability of an adhesive-substrate joint in the presence of water. We use predictions of molecular interaction energies to look at the interfaces between materials, from which surface energies are obtained which allow predictions of joint stability. In addition, work of adhesion is considered in order to understand the role of the adhesive composition upon the strength of adhesive joints. Finally, the mechanism of adhesion promoters for improving wet strength is explored.

Keywords: Molecular modelling; adhesion; wet strength; adhesion promoters; silanes

1. INTRODUCTION

The durability of an adhesive joint is highly dependent upon the surrounding environment. In particular, water can have a severe detrimental effect upon the strength of a joint [1]. There are many experimental tests available to determine the water sensitivity of an adhesive joint. However, these methods tend to be intrinsically dependent upon test conditions and history and it is difficult to obtain good correlation between tests and end-use performance. It would be highly desirable to have a consistent, generalised method for predicting the strength and, subsequently, the water sensitivity of an adhesive joint.

There are two main effects of water on the adhesive-substrate joint: cohesive and adhesive (interfacial). Cohesion is affected by absorbed water in the organic adhesive which acts to plasticize the material. The specific effect of small molecules, including water, on the visco-elastic properties of polymers (cohesion) have been discussed elsewhere [2], and therefore, no further discussion is presented. Adhesion is affected by the disruption of interfacial forces between the adhesive and substrate. We are concerned here with constructing a methodology based upon molecular modelling to simulate the interface between a substrate and an organic adhesive, the main objective of which is to allow the effect of water on the probable stability of an adhesive-substrate joint to be estimated.

Computational methods [3] are now available which relate the macroscopic properties of a material to its chemical and morphological structure, based upon the energies of interaction between molecules. Initial simulations given below demonstrate the effectiveness of these methods, where we present a comparison of calculated and observed cohesive properties for a series of common polymers. We then extend the model to study interfacial energies between materials, moving from small molecules ("surface tension") to polymeric adhesives and finally to inorganic substrates. By modelling the adhesive/water and substrate/water interactions separately, we show how work of adhesion for the individual interactions can be predicted. The stability of the adhesive-substrate joint can then be evaluated by a combination of our molecular modelling results and thermodynamic arguments.

The use of molecular modelling techniques to investigate an adhesive-substrate joint is analogous to the application of experimental methods for calculating surface and interfacial energy in conjunction with thermodynamics theory. Our model should, therefore, be viewed as a tool which could be applied to a wide range of problems associated with adhesion; such a topic for the application of our methods is that of adhesion promoters.

The durability of the adhesive joint can be improved dramatically by pre-treatment of the substrate with an organo-silane based adhesive primer [4, 5]. However, there is considerable debate as to the manner in which the primer aids in the resistance of the joint to the attack of water. The most likely explanation involves several processes including bonding of the primer to the substrate and exclusion of water at the interface by inhibiting water diffusion.The mechanisms by which these processes work are again unclear and in the final section of this paper we apply materials modelling techniques to investigate the effects of the primer on the adhesion process.

Finally, the authors stress that this paper is not intended as a detailed study of a particular adhesive system. Emphasis should be made with regard to the pragmatic approach of using commerically-available molecular modelling tools to complement experimental methods in the study of adhesion.

2. MODEL BASIS

The basis of our methods is in combining molecular modelling techniques with the thermodynamics approach to adhesion. In practice, parameters predicted from molecular modelling are utilised in thermodynamic expressions, which provide a unified basis for a general treatment of adhesion phenomena [6].

As previously stated, the strengths of adhesive joints are determined by a combination of cohesive and interfacial factors, where wet strength is particularly sensitive to interfacial effects. A thermodynamic analysis of adhesion is useful in that it considers the proceses of interfacial contact in a generalised manner, but also provides a quantifiable measure of adhesion: the work of adhesion. Thermodynamic models based on calculating the work of adhesion are, therefore, especially applicable for estimating the probability that an adhesive joint between an adhesive and a substrate might fail in the presence of water.

Work of adhesion is usually discussed in terms of the components of surface free energy [7, 8], where a greater work of adhesion gives a stronger adhesive bond. The origin of work of adhesion is in the intermolecular forces between the materials on either side of an interface, which can be split very roughly into van der Waals dispersion forces and polar forces between molecules. Both dispersion and polar components of energy must be quantified for an estimate of work of adhesion to be made. The work of adhesion, W_{12}, between surfaces with subscripts 1 and 2, is given by,

$$W_{12} = 2\left(\sqrt{\gamma_1^d \cdot \gamma_2^d} + \sqrt{\gamma_1^p \cdot \gamma_2^p}\right) \tag{1}$$

where γ^d and γ^p are for dispersion and polar components, respectively, of the surface free energy. The prediction of surface free energies for materials is, therefore, crucial to estimating work of adhesion, and can be achieved by the use of molecular modelling techniques.

Two main modelling methods were employed in our study of adhesion, namely molecular mechanics and molecular dynamics. Both are based on describing the energetics of a system as a function of the atom co-ordinates, using various two-body, three-body and four-body interactions. Each type of interaction is represented by a simple analytical expression, allowing rapid evaluation of energy and its derivatives. In molecular mechanics, minimisation procedures are used in conjunction with the potential energy expression to obtain the equilibrium geometry of a system. Molecular dynamics expands the method to include the kinetic energy of the system and, therefore, introduces the effects of motion and temperature. We utilise these methods to calculate the interaction energies between species, which are then manipulated to give the cohesive properties and, ultimately, the surface free energies of each material considered.

We note that all calculations were performed within the Cerius2 [9] software suite using the Universal Force-Field (UFF) [10], which proved satisfactory in reproducing polymer properties, as shown below. In addition, it is important to note that this modelling work calculates the energy of interaction between assemblies of molecules as a pseudo-continuum and does not try to model bulk energies from individual molecule interactions with a substrate. This allows molecular and continuum thermodynamic models to be combined.

3. COHESIVE PROPERTIES OF ADHESIVES

For an accurate evaluation of surface free energies, we must have a reliable method for modelling surfaces, which in turn is dependent on an ability to model the cohesive properties of the bulk materials. The method for calculating the cohesive properties of polymers is presented elsewhere [11, 12], and so only a brief description is given here. Quite simply, the cohesive energy is calculated as the difference in energy between an isolated polymer chain and the same chain in a 3-D periodic array; *i.e.* periodic boundary conditions (PBC) to represent the bulk material. Cohesive energy density is obtained from a knowledge of the cohesive energy and polymer cell volume, and subsequently allows the solubility parameter to be calculated.

Initial calculations were performed to determine the cohesive energy and solubility parameter for a series of common polymers in order to validate our computational model, the results of which are presented in Table I. As can be seen from the calculated cohesive energies, modelling is capable of reproducing the observed experimental data. In most cases, predicted values for the solubility parameter are slightly lower than the observed data, which was attributed to differences between the calculated and observed densities. The predicted solubility parameter for polydimethylsiloxane (PDMS) is higher than the observed value, the change in trend arising from differences in the flexibility and conformation of PDMS when compared with standard polymers such as polyethylene (PE) [13]. However, the results do suggest that the model for investigation of the bulk material can, with reasonable confidence, be extended to look at surfaces; in particular, to determine the work of adhesion between materials.

4. INTERFACIAL MODELLING

4.1. Interfaces Between Small Molecules

Work of adhesion can be defined as the work required to separate two materials from an interface to create two surfaces, with an energy

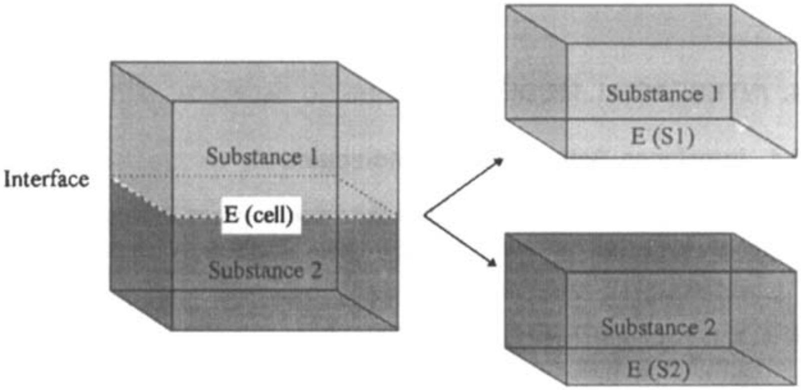
TABLE I Calculated (molecular modelling) and observed (experimental) cohesive properties of polymers

	Calculated		*Expt**	
Polymer	E_{coh} (kJ/mol)	δ $(J^{1/2}cm^{3/2})$	E_{coh} (kJ/mol)	δ $(J^{1/2}cm^{1/2})$
polyethylene	8.7	14.8	8.2 – 9.6	15.8 – 17.1
polyvinylchloride	16.0	18.1	16.7 – 22.1	19.2 – 22.1
polystyrene	30.6	16.9	29.7 – 35.4	17.4 – 19.0
polymethylmethacrylate	52.9	23.6	29.9 – 59.4	18.6 – 26.2
polydimethysiloxane	16.2	15.2	16.0 – 16.9	14.5 – 15.0
polycarbonate	83.8	18.7	83.0 – 93.0	19.8 – 20.9

*van Krevelen, D. W., *Properties of polymers* (Elsevier, Oxford, 1990).

expense due to the loss of the interface. We model the work of adhesion according to this concept. A layered periodic cell is constructed where one-half of the cell is occupied by one substance, and the opposite half of the cell by a second substance creating a pseudo-infinite interface. Molecular dynamics and energy minimisation procedures are then used to create an energy-equilibrated system. Each layer is removed in turn from the cell and the interfacial energy calculated as the difference between the energy of the whole cell and the sum of the individual layers per unit interface area, as depicted in Figure 1. Our method is analogous to the calculation of surface free energies using experimental methods [7, 8].

Initial studies focused upon calculating the interfacial energies between small molecules. For example, Table II presents a comparison of calculated (using the molecular modelling method outlined above) and experimental energies for the interaction between water and methylene iodide. The calculated interfacial energies between water and methylene iodide are clearly in good agreement with experimental



Interfacial energy = E (cell) - Const. [E(S1)+E(S2)]

(All energies are per unit surface area. The constant is equal to the number of new surfaces created when the cell is split.)

FIGURE 1 Schematic of the method used to calculate interfacial energies. The energy of the interface is given as the difference in energy between the cell containing both substances 1 and 2 interacting across the interface, and the total energy of substances 1 and 2 at infinite separation.

TABLE II Calculated and experimental values for the surface free energy (dispersion, polar and total) between water and methylene iodide

Component	*Calculated* *(mJ/m^2)*	*Expt** *(mJ/m^2)*
dispersion (γ^d)	57	66
polar (γ^p)	19	16
total γ	76	82

*van Krevelen, D. W., *Properties of polymers* (Elsevier, Oxford, 1990).

data, and show the validity of our approach to give reliable predictions concerning the interactions between different materials at an interface. Indeed, methylene iodide and water are often used experimentally as reference substances in interfacial tension experiments to measure surface free energy. The results of such tests can then be used to calculate the components of surface free energy of polymeric adhesives.

4.2. Adhesive-Substrate Surface and Interfaces

The method for modelling interfacial energies of small molecules can be extended and applied to the investigation of the adhesive-substrate interface. A typical example of a polymer adhesive on a metal oxide substrate is PMMA (polymethylmethacrylate) on corundum (aluminium oxide), and is used as a model for our study. Previous investigations [14] have used *ab initio* quantum mechanical methods to look at specific interactions between individual monomer units of PMMA with metal and metal-oxide surfaces. However, the thermodynamic approach to adhesion necessitates the use of assemblies of molecules, as employed in our studies.

The surface free energy of any material can be estimated, provided that we can accurately model the interaction between that material and another material with known surface energies. The surface free energies obtained from our water/methylene-iodide calculations can be utilised for reference to estimate the surface free energies of PMMA and substrate. First, the work of adhesion between the substrate or adhesive and the small molecules is calculated from the interaction energies. The expression given in Equation (1) is then used to substract the surface free energy of the small molecules from the interfacial energy, thereby giving the surface free energy of the unknown.

Generation of the polymer surface is comparatively straightforward, and Table III presents a comparison between calculated and experimental surface free energies for PMMA, where the calculated values were obtained from modelling the interaction of PMMA with water, depicted in Figure 2.

Modelling the surface of the inorganic substrate requires more careful consideration. In particular, caution must be exercised when parameterising the inorganic substrate to ensure the use of appropriate charges for the atoms at a surface, since polar forces dominate the interfacial energy for many such materials. The charges for corundum were calculated using the charge equilibration (Qeq) method within Cerius2, the charges for the surface ions (Al ~ 0.4, O ~ -0.3) being approximately half the value of the bulk ions (Al ~ 1.0, O ~ -0.6). We note that the charges were not allowed to vary during the period of any calculation.

A surface of the substrate is created by cleaving the material in the required plane, resulting in a 2-dimensionally periodic pseudo-infinite surface. Figure 3 shows an aluminium oxide (corundum) surface created by cleaving the bulk material in the 100 plane. We note that, when investigating crystal surfaces, the atomic structure at the surface of a material can vary significantly from that in the bulk [15]. The UFF proved unsatisfactory with regard to producing a relaxed surface structure and so, for the purposes of demonstrating our method, the ions were held fixed in their original positions. A quantitative analysis of corundum is, therefore, not possible; nevertheless, our model should provide qualitative data which is sufficient to allow comparison between the interaction of different materials with a metal-oxide substrate. Note also that we do not include oxidation products in our calculations.

TABLE III Calculated and experimental values for the surface free energy (dispersion, polar and total) of PMMA

Component	*Calculated (mJ/m^2)*	*Expt* (mJ/m^2)*
dispersion (γ^d)	25.1	29.6
polar (γ^p)	12.6	11.5
total γ	37.7	41.1

*van Krevelen, D. W., *Properties of polymers* (Elsevier, Oxford, 1990).

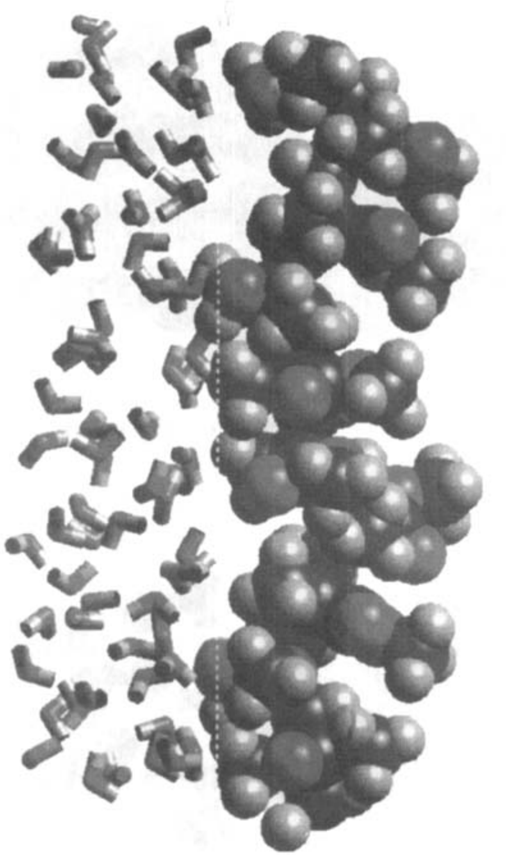


FIGURE 2 The surface free energy of the polymer adhesive can be calculated from knowledge of the interaction with reference small molecules. Here we model the interaction of water with PMMA. (carbon – green, oxygen – red, hydrogen – grey). (See Color Plate I).

The substrate and polymer interfacial models differ slightly from the model used for the water/methylene-iodide calculations in that the systems are only 2-D periodic. Following the creation of the surface, as outlined above, the organic material is then added such that it forms a complete layer over the entire surface area of the substrate, see Figure 4. The work of adhesion is calculated as the difference in energy between the materials at close proximity, thus forming an interface, and the combined energy of the individual materials at infinity

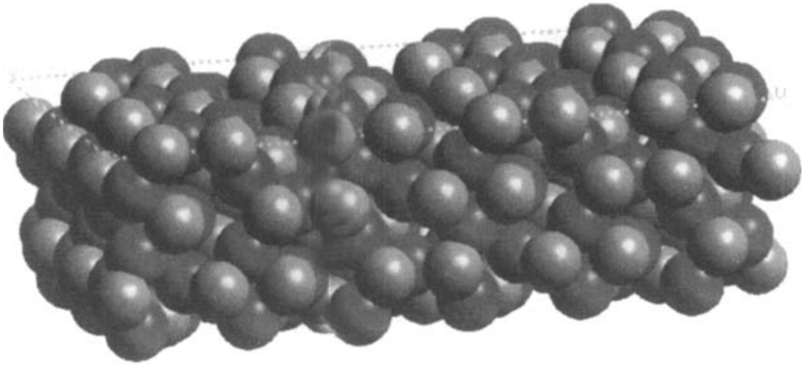


FIGURE 3 Schematic of the aluminium oxide (corundum) surface, created by cleaving the bulk material in the 100 plane. (aluminium – light brown). (See Color Plate II).

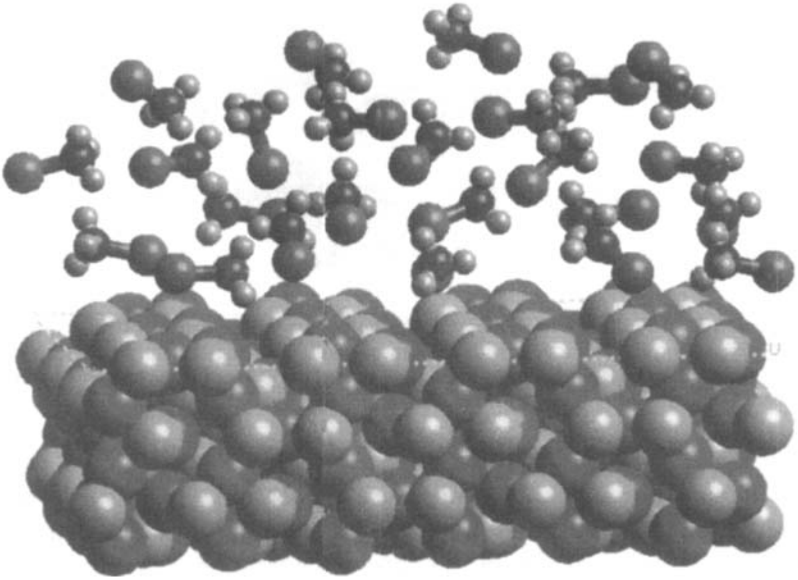


FIGURE 4 We estimate the surface free energy of an inorganic substrate by using reference small molecules. For example, here we model the work of adhesion between corundum and methyl iodide. (See Color Plate III).

separation. The surface free energies for all the materials studied are presented in Table IV, and can now be used to determine the water sensitivity of an adhesive-substrate joint, which in our case is represented by PMMA on corundum.

4.3. Wet Strength

The previous section has shown that the energy of interfaces between small molecules or polymeric adhesives and substrates can be quantified by molecular modelling. The technologically interesting step then is to use these energies in a conventional thermodynamic treatment of the water sensitivity of adhesive joints. The work of adhesion between the adhesive and the substrate has to be greater than the work of adhesion between water and both the adhesive and substrate surface for the joint to be stable in the presence of water. For example, the total work of adhesion for PMMA on our model corundum surface in the presence of water is predicted to be negative ($-108\,\mathrm{mJ/m^2}$), such that the joint would be sensitive to water. The method thus allows prediction of the stability of an adhesive-substrate interface in the presence of water, through the calculation of surface free energies for any given material.

However, in the event that the model predicts sensitivity to the presence of water, if does not provide information regarding the mechanism of interfacial failure. Therefore, in an attempt to further our understanding of interfacial failure, we have employed molecular dynamics methods to investigate the attack of water at an organic-substrate interface.

TABLE IV Values for the surface free energy (dispersion, polar and total) of the materials studied

Material	*Surface free energy (mJ/m^2)*		
	γ^d	γ^p	*total* γ
Water[a]	21.8	51.0	72.8
Methylene iodide[a]	49.5	1.3	50.8
PMMA	25.1	12.6	37.7
Metal-oxide substrate	137.0	263.4	400.4

[a] van Krevelen, D. W., *Properties of polymers* (Elsevier, Oxford, 1990).

5. MODELLING INTERFACIAL FAILURE

A molecular dynamics study has been performed to model the effect of water on an organic-substrate interface. The model shown in Figure 5. is constructed, where a layer of pentane molecules is adsorbed onto the substrate surface, followed by the introduction of a volume of water above the organic layer. An additional layer of material, in this case polyethylene, is placed above the water and held fixed throughout the simulation to stop the water from "evaporating". A simulation (NVT method) is then performed, allowing motion of only the pentane and water molecules for a period of 50ps at a temperature of 300K. The resulting trajectory file can then be studied to give a time-dependent analysis of the attack of water at an organic-substrate interface.

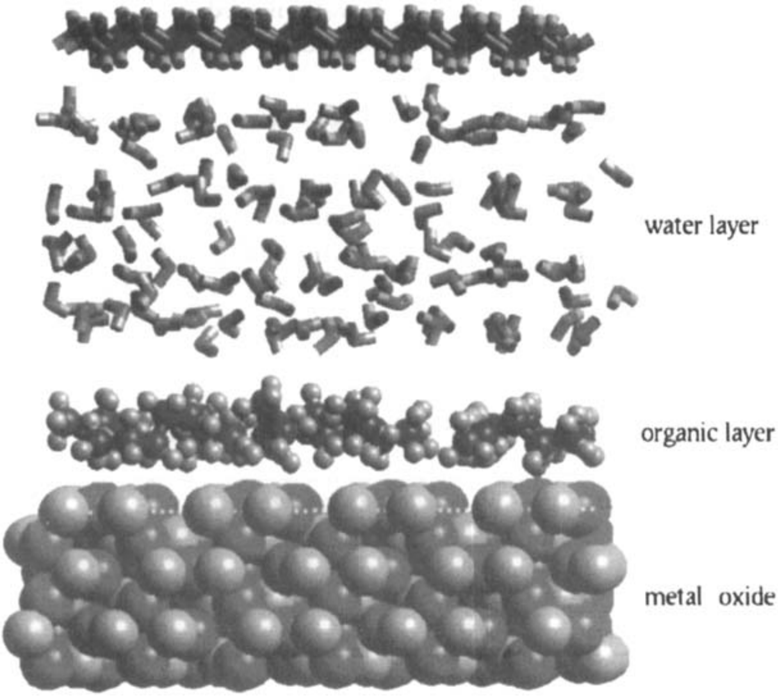


FIGURE 5 Model used for molecular dynamics (MD) study of the water sensitivity of an organic-substrate interface. (See Color Plate IV).

The position of all the molecules at the end of the simulation is shown in Figure 6, and clearly indicates the replacement of the adsorbed pentane molecules at the substrate surface by water. More especially (Fig. 6b) we see the formation of several "clusters" of water molecules adsorbed onto the substrate with a number of the pentane molecules effectively desorbed. The mechanisms by which this process occurs can be obtained from an analysis of the trajectory file. The initial step appears to be a desorption of the organic, usually by the lifting of part of the chain from the surface. Water is then absorbed onto the substrate, effectively replacing part of the organic layer. The process continues by further desorption of the organic to the point, as shown in Figure 6a, where several pentane molecules are standing upright on the surface. Additional water molecules are attracted to water

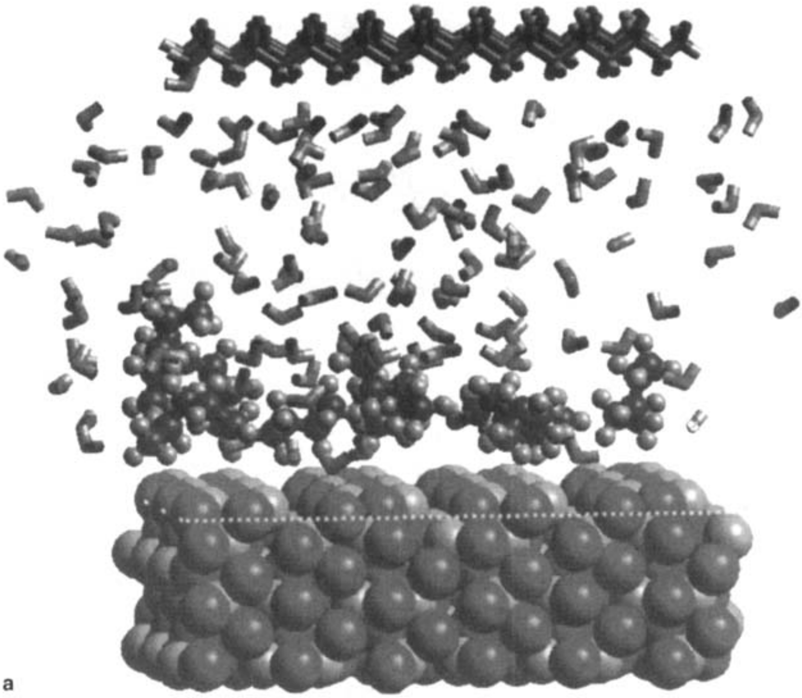


FIGURE 6 Configuration of the final step in the MD simulation, (a) side-on view and (b) view looking down onto the surface where only the molecules (organic species and water) in close proximity to the substrate surface are shown (substrate surface represented by the light brown polyhedra). (See Color Plate V).

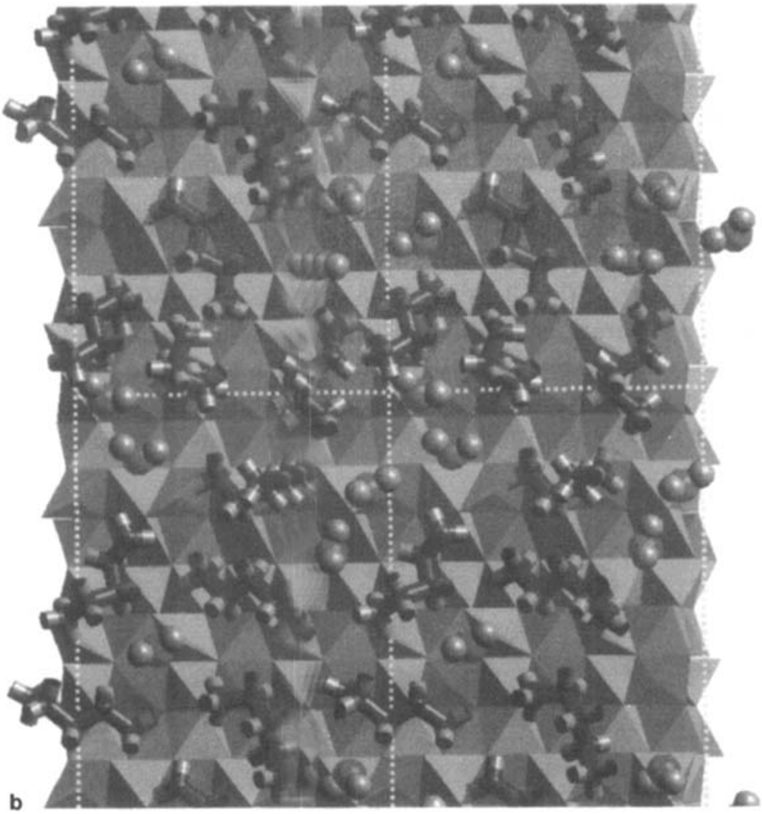


FIGURE 6 (Continued). (See Color Plate V).

at the surface *via* hydrogen bonding and small clusters are formed which force voids to be created in the organic layer. If allowed to continue, we would expect continual replacement of the organic species by water at the substrate surface to proceed to the point where the organic-substrate joint has effectively failed, as suggested by the calculated works of adhesion. We note that prior to joint failure there must be a progressive weakening of the joint as a result of water at the interface.

6. SILANE-BASED ADHESION PROMOTERS

The final stage of our work is to determine the effect of adhesion promoters on the durability of a polymer adhesive-inorganic substrate joint, in particular to study silanol coupling agents which are often used to improve the water resistance of adhesive joints. Important to the effectiveness of the silanol adhesion promoter is its bifunctionality, where there is a highly polar end which can bond to a polar substrate and an organic "tail" which interfaces with the polymeric adhesive. The question asked in this work was whether the silanol needed to bond chemically with the substrate in order to improve wet strength.

First, a very simple silanol structure, *n*-propyl silanol, $CH_3(CH_2)_2Si(OH)_3$, was constructed, and the surface free energy of the bulk material was calculated using the method outlined above. We note that to ensure accurate polar interactions the charges for the silanol species were calculated using quantum mechanical methods (MOPAC-PM3). The predicted values for the bulk material are presented in Table V, and found to be higher in magnitude than observed data for $CH_3(CH_2)_2Si(OCH_3)_3$, also shown in Table V. However, the difference in surface energies is not unreasonable owing to the slight variation in composition between the two molecules. More importantly, the ratio of dispersion to polar energies is consistent and suggests that the organic component of the *n*-propyl silanol will dominate the properties in the bulk material. Based upon these results for the bulk material, the silanol compound would not be effective as an adhesion promoter and, therefore, additional forces must come into play when in the environment of the ionic substrate surface.

In an attempt to model these effects and simulate the application of the promoter to the surface, an assembly of *n*-propyl silanol molecules was adsorbed onto the substrate surface to form a monolayer. The system was then equilibrated using a series of molecular dynamics and energy minimisation steps, with a typical model of the promoter on the substrate shown in Figure 7. The process was repeated several times

TABLE V Values for the surface free energy (dispersion, polar and total) of silane groups

^{a}*Material*	*Surface free energy (mJ/m²)* γ^d	γ^p	*total* γ
n-propyl silanol (bulk-predicted)	27.2	19.8	47.0
n-propyl silanol (observed)*	18.1	13.6	31.7
n-propyl-silanol (obtained from silanol-substrate interaction)	84.0	424.8	508.8

*Plueddemann, E. P. *Silane Coupling Agents* (Plenum Press, New York, 1982).

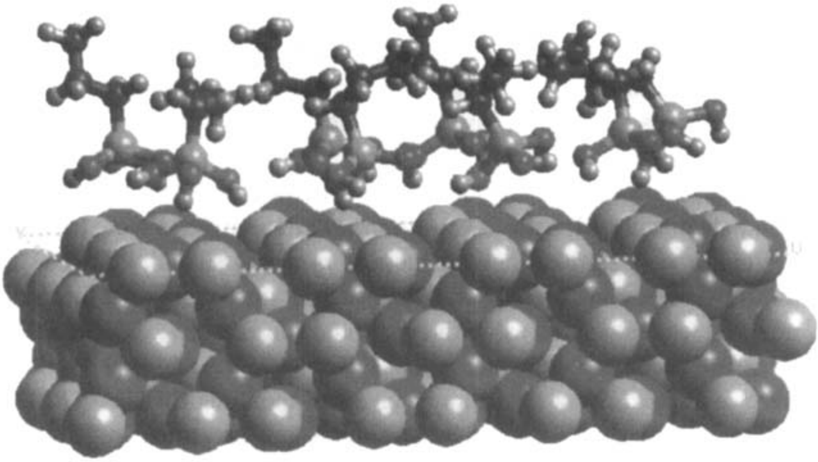


FIGURE 7 Propyl silanol molecules adsorbed onto the substrate surface. Note that in each case the silanol end of the molecule is in closest proximity to the surface. (See Color Plate VI).

and, provided there was a complete monolayer coverage of the surface by the promoter, a configuration similar to that shown in Figure 7 was obtained. The energy of the silanol-substrate interface can now be calculated and, when combined with consistent models for the silanol/water and water/substrate interfaces, a full thermodynamic calculation of the work of adhesion in the presence of water can be obtained.

The surface free energies for the promotor on the substrate surface are vastly different to those of the bulk material, see Table V, where the highly polar silanol group now dominates due to the strong affinity with the ionic substrate. The affinity is indicated by the model, Figure 7, where the silanol group for each primer molecule is in closest proximity to the substrate surface. These predicted values obviously represent an extreme case were the silanol groups form a single monolayer with all the groups oriented in a similar manner. Moreover, observation [4] has shown that a broad range of surface tensions can be obtained, dependent upon factors such as the method of application of the primer to the substrate.

Using the predicted surface free energies for the silanol obtained from the interaction with the substrate, the work of adhesion in the presence of water is found to be strongly positive (560 mJ/m^2). We stress that no chemical bonding was used in the energy calculations, suggesting that the silanol group is intrinsically stable on a polar substrate in the presence of water. The strong polar, physical attraction between primer and ionic substrate is, therefore, an important factor in their application and would precede the formation of chemical bonds. Indeed, the strong interaction between primer and substrate should facilitate the formation of chemical bonds.

Additional aspects which need to be addressed regarding the use of silane-based compounds as adhesion promoters are the functionality and length of the organic tail. Many of the primers in use have a particular functional group added to the end of the organic tail, which is designed to ensure a strong interaction of the primer with the adhesive. The length of the organic tail is critical to the effective use of the primer as an adhesion promoter. Firstly, the application of the primer to the substrate surface will be impeded by too lengthy an organic tail due to difficulties in dispersing the primer. In addition, the bifunctional, polar to non-polar, nature of the primer may result in the formation of micelles which again will hinder the application of the primer. Secondly, the packing of the tail above the substrate acts to inhibit the approach of water to the interface, with an optimum length dependent upon both the surface area of the silanol group and also the angle of inclination of the chain to the surface. The investigation of these factors is an obvious next step for future work in materials modelling of silane-based adhesion promoters.

7. CONCLUSIONS

We show how a combination of molecular modelling and thermo*dynamic* expressions can be used to understand the mechanism of adhesion between materials. Several points have arisen from the work.

1. Quantitative predictions of the energy at interfaces, in conjuction with thermodynamic models of adhesion, allow us to model the strength of adhesive joints using the work of adhesion.
2. A dynamics study of the attack of water at an organic-substrate interface gives valuable insight into the mechanisms involved in the adhesive failure of the joint.

3. Our paper illustrates how the sensitivity of adhesive joints to water can be modelled, and shows great promise for the development of new materials as adhesion promoters.

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