ELSEVIER

Polymer 43 (2002) 963–969

polymer

www.elsevier.com/locate/polymer

Computer simulation of structure and properties of crosslinked polymers: application to epoxy resins[☆]

Irene Yarovsky[a,*], Evan Evans[b]

[a]Department of Applied Physics, RMIT University, GPO Box 2476V, Melbourne, Vic. 3001, Australia
[b]BHP Steel Research Laboratories, Old Port Road, Port Kembla, NSW 2505, Australia

Abstract

In this work, a methodology has been developed for construction of atomistic models of crosslinked polymer networks. The methodology has been applied to low molecular weight water soluble epoxy resins crosslinked with different curing agents that are being considered for use as a primer coating on steel. The simulations allowed the crosslink density and the amount of free crosslinking sites in the coatings to be predicted. Shrinkage of the resin upon curing was reproduced by the simulation. In addition, the barrier properties of the model coatings were estimated. The interface between an inorganic substrate and cured epoxy resin has been constructed and the strength and molecular mechanisms of adhesion have been revealed. The developed methodology has a potential to significantly impact on the design and development of new coatings with improved barrier and adhesion properties. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Molecular simulation; Crosslinked polymers; Epoxy resin

1. Introduction

A search for new improved components for coating systems requires a better understanding of the structure/property relationships of the materials. Although some properties of coating systems can be obtained experimentally, an ability to predict properties of new coatings prior to laboratory synthesis will significantly facilitate new coating design. Recent developments in molecular simulation techniques provide a tool for predicting the bulk and interfacial properties of organic coatings, a review can be found, for example in Ref. [1]. In the present study, these techniques have been applied to the prediction of physical properties of low molecular weight crosslinked resins that are being considered for use as a primer coating on steel.

The goal of this work was to develop a methodology for construction of molecular models of crosslinked polymer networks with application of this methodology to low molecular weight water soluble epoxy resins cured using different crosslinking agents. This will enable a prediction of the crosslink density and the amount of free crosslinking sites in the alternative coating materials thus contributing to a better understanding of molecular mechanisms of the coatings performance. A simulation can also be designed to reproduce shrinkage of the resins occurring due to the crosslinking reactions in order to estimate the stress introduced in the coatings material by the curing process. In addition, the diffusion rate of water and oxygen through the theoretical coatings can be estimated to assess their barrier properties using molecular dynamics (MD) simulations, examples can be found in Refs. [2–10]. The interfaces between inorganic substrates and cured epoxy resin coatings can be constructed and the strength and molecular mechanisms of adhesion revealed as described in Ref. [1].

Overall, an ability to theoretically predict properties of crosslinked polymers would have a significant impact on the design and development of new coatings with improved barrier and adhesion properties [11].

2. Molecular model of the epoxy primer

Epoxy primer modelled in this study, in reality consists of several major components: epoxy resin, crosslinking agent, pigment, binder, solvent, and other additives. However, the molecular model of a water based primer considered in this work was restricted to the resin and crosslinker components, with water as a solvent. Thus, this work represents an initial step towards developing more comprehensive realistic

---

[☆] This paper was originally submitted to *Computational and Theoretical Polymer Science* and received on 23 June 2001: received in revised form on 24 August 2001: accepted on 3 September 2001. Following the incorporation of *Computational and Theoretical Polymer Science* into *Polymer*, this paper was consequently accepted for publication in *Polymer*.

[*] Corresponding author. Tel.: +61-3-9925-2571; fax: +61-3-9925-5290.
E-mail address: irene.yarovsky@rmit.edu.au (I. Yarovsky).

PII: S0032-3861(01)00634-6

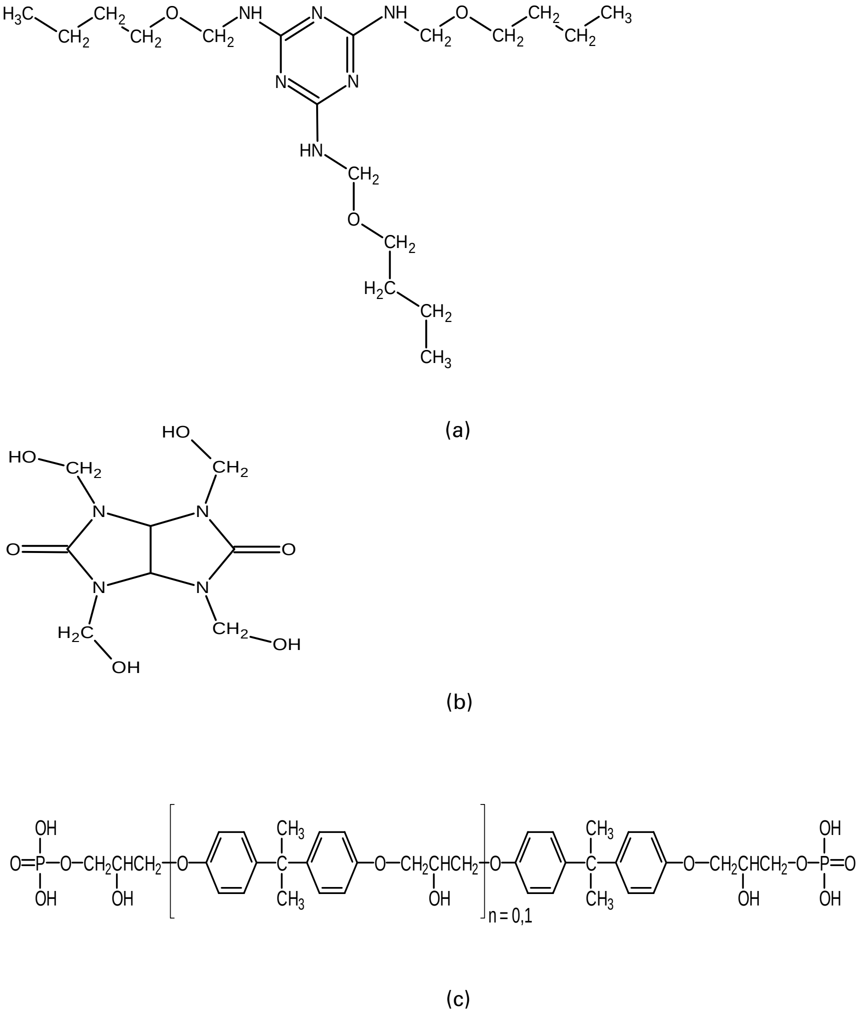

Fig. 1. Structure of the resin and crosslinker molecules: (a) CYMEL 1158: tributoxymethyl-melamine, (b) CYMEL 1172: tetramethylol glycoluril, (c) Phosphated epoxy resin: P0 − $n = 0$; P1 − $n = 1$.

models of coatings materials including other major components. In particular, the models constructed in this work did not include solid particle components such as pigments and fillers, which would require significantly larger scale models that are presently out of scope of the atomistic simulations.

2.1. Structure of the resin and crosslinker molecules

Fig. 1 represents the structural formulae of the resin and crosslinker molecules used in this simulation. Low molecular weight phosphate modified epoxy resins have been investigated for use as water based primer resin components. Particularly, the resins of polymerisation degrees of 0 (P0) and 1 (P1) were considered in the molecular modelling study. Melamine resins are normally used as curing agents, one of the commonly used types being CYMEL 1158 crosslinker (tributoxymethyl melamine, average polymerisation degree equals 2.6, Fig. 1(a)). The CYMEL 1172 crosslinker (tetramethylol glycoluril, Fig. 1(b)) has been recently suggested for use with P1 type epoxy resins. It has been found that CYMEL 1172 improves primer properties compared to traditional melamine crosslinkers [11]. Therefore, three model systems (Table 1) comprising alternative types of resin (P0, P1) and crosslinker (CYMEL 1172 and 1158) have been considered here to investigate the effects of composition on primer properties. Size of the model systems varied between 1000 and 1300 atoms per unit cell depending on composition. Number of molecules is specified in column 3 of Table 1.

2.2. Crosslinking reactions

The functional groups of the epoxy resin involved in the crosslinking reactions are hydroxyls. The reactivity of the hydroxyl groups along the polymer chain can be expected to be different. In particular, based upon the steric considerations, the most reactive would be the OHs of the phosphate group, then the end-chain OH group and then the mid-chain OH group (Fig. 1(c)).

The curing occurs at elevated temperature (230–240°C)

Table 1
Parameters of the simulated systems and the crosslink density obtained

System	Resin/crosslinker weight ratio	Resin/crosslinker mole ratio	Density of crosslinker reactive groups, no. per unit volume ($\times 10^{-4}$ groups/Å^3)	Density of crosslink bonds created, no. per unit volume ($\times 10^{-4}$ groups/Å^3)	Percentage of unreacted crosslinker reactive sites (%)
P0 + 1158	78:22	12:2	8.8	8.8	0
P1 + 1158	79:21	8:2	8.7	6.0	30
P1 + 1172	85:15	10:5	15.2	7.6	50

by the following key reactions involved in the crosslinking process:

CYMEL 1172:

$$\sim \mathrm{OH} + \mathrm{HOCH_2}\overset{|}{\mathrm{N}}\text{–M} \rightarrow \sim \mathrm{OCH_2}\overset{|}{\mathrm{N}}\text{–M} \qquad (\text{–}\mathrm{H_2O})$$

CYMEL 1158:

$$\sim \mathrm{OH} + \mathrm{ROCH_2}\overset{|}{\mathrm{N}}\text{–M} \rightarrow \sim \mathrm{OCH_2}\overset{|}{\mathrm{N}}\text{–M} \qquad (\text{–ROH})$$

where $R = C_4H_9$, M is the crosslinking agent.

In addition, the curing agent self-crosslinking may take place. This reaction is not, however, considered to be a major reaction and is accounted in the modelling study by using the melamine trimer of the CYMEL 1158 agent.

3. Algorithm for atomistic simulation of structure and properties of crosslinked polymers

The process of atomistic simulation of crosslinked polymer systems and their properties involved several steps described below in full detail.

3.1. Modelling the crosslinked system

Step 1: A physical mixture of the resin and crosslinker molecules of an experimental weight/molar ratio has first been simulated. The Amorphous Cell procedure described elsewhere [12,13] has been used to generate ten atomistic models of each resin/crosslinker system. The resulting 3D periodic molecular systems were equilibrated using the constant volume/constant temperature (NVT ensemble) MD simulation [1]. To imitate the curing regime, the systems were initially heated up to 600 K for 100 ps MD simulation and then equilibrated at 300 K for another 200 ps of MD. The intra and intermolecular interactions within the systems were determined by the pcff forcefield [14,15] distributed by Accelrys.

Step 2: The resulting physical mix of the resin and crosslinker molecules has then been analysed in order to identify the reactive sites in close proximity. These sites were considered the most probable to participate in the crosslinking reactions according to the steric considerations. The reactivity order for the resin hydroxyl groups has been taken into account, i.e. given similar interatomic distance the priority 'to react' has been given to the phosphate group oxygen, followed by the end chain and then mid-chain hydroxyls. The interatomic distance of 6 Å has been taken as a reaction cutoff distance, i.e. the groups separated by the longer distance were considered non-reacting. This cutoff distance has been chosen so as not to increase the strain in the molecular system too severely upon crosslinking. Although the choice of a cutoff distance has been somewhat arbitrary, it was based on several trials of various distances and was considered the most appropriate.

Step 3: The reaction sites identified in the previous step have been 'chemically reacted', i.e. the new chemical bonds have been created while water (in the case of CYMEL 1172 system) or butanol (in the case of CYMEL 1158 system) molecules were eliminated (removed from the systems). The resultant molecular systems have then been equilibrated again using the NVT MD process for 200 ps at 300 K. This returned the newly created bonds to the equilibrium values and removed the strain imposed by the bond breaking/creating process. This process does not reproduce the shrinkage of the epoxy upon curing. The shrinkage has been separately simulated by the constant pressure/constant temperature (NPT ensemble) MD as described in Section 3.2. However, the process described here allows one to build the crosslinked systems and the crosslink density (i.e. degree of curing) to be estimated as well as it prepares the systems for subsequent NPT simulation as described in Section 3.2.

3.2. Shrinkage of the epoxy resin upon curing

Shrinkage (volume reduction) of the resins occurring during the curing process may effect adhesion of the film to the substrate because high levels of shrinkage induce considerable stress in the cured film. In order to reproduce shrinkage of the epoxy system that occurs during curing, the NPT MD was employed. Atmospheric pressure was applied to the 3D periodic systems constructed as described in Section 3.1 and the curing temperature of 600 K was used. The MD process continued until the volume of the systems reached its equilibrium value, which took about 100 ps. After the equilibrium was achieved the MD at 300 K was continued for 1 ns to collect the properties of the systems. For each composition, the procedure has been repeated and the properties have been averaged over all systems built by the Amorphous Cell method thus producing the averages over 10 ns of real time.

3.3. Barrier properties

The barrier properties of organic coatings, i.e. the transport of penetrant molecules (in particular, those of water and oxygen) through the coatings is important for anticorrosion protection of the underlying metal substrate. The permeability is the most important quantifier of the transport of penetrant molecules through polymers. The barrier performance of a polymer can be defined as its resistance to the transport of penetrant molecules, i.e. as the inverse of its permeability.

The permeation of small molecules through polymers usually occurs by the solution–diffusion mechanism which has two key steps [16]. The penetrant molecule is first sorbed by the polymer, i.e. dissolves in the polymer matrix. Then the permeability is controlled by diffusion of the small molecule through the polymer. The permeability is equal to the product of the diffusivity (diffusion coefficient) and solubility.

In this work, the diffusion constants for small molecules in a polymer matrix has been calculated from long term MD. It should be noted that the low molecular weight of the water soluble polymers (or rather low oligomers) made it possible to estimate diffusion constants of water that would not otherwise be possible due to the limited time scale of the computer simulation. The absolute values of the calculated diffusion constants should not, however, be considered for direct comparison with experimental values due to several assumptions used in the idealised models of the coatings and the potentials (forcefield) used to describe interatomic interactions. Therefore, our goal is to check whether the calculated values can be used for comparison of *relative* diffusivities of small molecules in the low molecular weight water soluble polymers of different composition.

The diffusion coefficient of a component in a molecular mixture can be calculated from the Einstein relation [17]:

$$D = \frac{1}{6N} \lim_{t \to \infty} \frac{\mathrm{d}}{\mathrm{d}t} \sum_{i=1}^{N} \langle [\vec{R}_i(0) - \vec{R}_i(t)]^2 \rangle \qquad (1)$$

where R_i is the position of the molecule centre of mass, N is the number of the molecules of a given type, and the broken brackets denote averaging over all choices of time origin. This quantity has been calculated directly from MD trajectory over a relatively long simulation time period (1 ns).

Several factors play the key role in determining the relative diffusivity of different penetrant molecules permeating a polymer by the solution–diffusion mechanism. First of all, it is the free volume available for the penetrant molecule to traverse the polymer. It should be noted that in contrast to the total free volume in the polymer matrix, the free volume available for diffusion is a function of the molecular size of a penetrant. Secondly, the cohesive forces between the polymer chains affecting the chain mobility are also crucial since there exists a correlation between the chain mobility (rigidity) and diffusion constants of penetrant molecules [18]. Finally, the diffusivity (and solubility) can be affected very significantly by the strength of the interactions between the penetrant molecule and the structural units in the polymer chains, for example by the specific interactions such as hydrogen bonding. These molecular effects can be revealed from the atomistic simulation of polymer systems in addition to the relative values of diffusion constants.

3.4. Adhesion

The crosslinked system simulated as detailed in Section 3.2 has been layered with a solid surface (alumina) as described in Ref. [1]. The MD procedure has been applied to the resultant 2D periodic interface allowing the adhesion between the two surfaces to be simulated. Constant volume, constant temperature MD has been applied to the interface divided by a vacuum spacer between the two layers to allow some space for molecular relaxation. In the starting configuration, the polymer layer has been compressed in order to achieve the correct density in the final system. The MD simulation has started at the temperature of 600 K to allow for a better relaxation of the molecular system for 100 ps. Then the system has been cooled down to 300 K and equilibrated for another 200 ps. The last 100 ps for each system (i.e. the total of 1 ns over 10 structures for each composition) have been used for analysis of the resulting equilibrium molecular geometry and calculation of the energetics.

The work of adhesion has been calculated from the relationship of Dupré [19]:

$$W_a = \gamma_A + \gamma_B - \gamma_{AB} \qquad (2)$$

where γ_A and γ_B is specific surface free energy of phases A and B, respectively, (surface tension), and γ_{AB} is specific interfacial free energy of contacting phases A and B (interfacial tension). These quantities have been directly obtained from the MD simulations of the bulk, surface and interfaced materials and the absolute values are based on the (pcff) forcefield used in the simulation [1,5,6]. Therefore, only the relative values of the work of adhesion can be used for comparison of proposed coatings.

4. Results and discussion

Following the above procedures structural, thermodynamic and transport properties of the three model coatings systems have been obtained. The details of the simulated systems are summarised in Table 1. The crosslink density, the amount of unreacted crosslinking sites and shrinkage upon curing have been calculated for the systems simulated. In addition, the barrier properties of the bulk material have been estimated. The interface between cured epoxy systems and alumina has also been modelled and molecular mechanism

Table 2
Percentage volume reduction and final density in the simulated systems following the NPT MD

System	Volume reduction (%)	Density (g/cm^3)
P0 + 1158	12.03	1.24
P1 + 1158	5.30	1.19
P1 + 1172	5.35	1.24

of adhesion has been suggested. Detailed description of the results for each property is given in the following sections.

4.1. Crosslink density

The crosslink density and amount of unreacted crosslinker groups in the simulated molecular systems are summarised in Table 1. It can be seen that in the P0 + 1158 system all crosslinker reactive sites formed covalent bonds with the resin while in the P1 + 1158 system only 70% of crosslinker reactive sites have reacted. This result can be explained by the fact that in the larger P1 resin molecule the reactive groups are not as well accessible as in the smaller P0 molecule. This is especially important if at least one reactive site on the resin molecule has already reacted. In this case, the other sites become less mobile, i.e. less probable to react, due to partial immobilisation of the resin and the crosslinker. Since the CYMEL 1158 crosslinker is fairly bulky, it can be less sterically accessible to the larger P1 molecules than to the more mobile P0 molecules. This result is experimentally confirmed by our preliminary NMR studies demonstrating that the accessibility of the reactive groups in bulkier crosslinkers is lower compared to the smaller ones. This was apparent from differences in intensity of the unreacted hydroxyl groups of the crosslinker [20]. In addition, for the same resin:crosslinker weight ratio, there is more P0 molecules than P1 molecules per the same number of crosslinker molecules due to the weight difference between P0 and P1 (Table 1). Therefore, there is more of the smaller and, hence, mobile resin molecules available for linking in the P0 system compared to the P1 system. As a result, all available crosslinker sites have been reacted in the P0 system resulting in the highest possible crosslink density of all systems (Table 1).

In the P1 + 1172 system only 50% of available crosslinker sites reacted with the resin (Table 1). However, this resulted in the higher crosslink density than that achieved in the P1 + 1158 system. This is because there is more CYMEL 1172 than 1158 molecules present in the system of similar resin/crosslinker weight ratio due to the lower molecular weight of CYMEL 1172. Since each CYMEL 1172 molecule has four reactive groups (while CYMEL 1158 trimer has five), the larger amount of CYMEL 1172 molecules results in almost twice as high concentration of crosslinker reactive groups in the CYMEL 1172 system compared to the CYMEL 1158 systems (Table 1). Moreover, due to the lower molecular weight and compact size the CYMEL 1172 molecules are more mobile and would be able to reach the resin reactive sites easier than the CYMEL 1158 molecules. Therefore, the resultant crosslink density in the P1 + 1172 system is almost as high as in the fully crosslinked P0 + 1158 system. At the same time, half of the CYMEL 1172 reactive sites are left unreacted which enables them to contribute to cohesive as well as adhesive properties of the material. This combination of properties can explain better experimental performance of the P1 + 1172 system compared to other primers [11].

4.2. Shrinkage of the epoxy resin upon curing

The results of the volume reduction upon crosslinking in the studied systems are presented in Table 2. It can be seen that in the fully crosslinked P0 + 1158 system the most significant volume reduction has been achieved. This result can be explained by the fact that the amount of free volume created by evaporation of butanol molecules during the crosslinking reaction was the highest in this system. Therefore, to achieve the experimental density the considerable shrinkage must occur. In the partially crosslinked P1 + 1158 system the volume reduction was lower which is due to less free volume created upon crosslinking. The equilibrium density is also slightly lower which may result in poorer barrier properties of the less dense systems.

In the P1 + 1172 system, the volume reduction was less than in the P0 + 1158 system and similar to the P1 + 1158 system but the equilibrium density was higher compared to the latter system. This result can be due to the higher crosslink density and suggests better barrier properties of this system compared to the other systems studied.

It should be noted that the calculated densities compare well with the experimental values [11].

4.3. Mobility of water and oxygen in the crosslinked systems

The values of the calculated diffusion constants for water and oxygen molecules in the crosslinked systems are presented in Table 3. For each model system, three cases have been considered. In the first and second cases, all free volume available in the systems has been filled by either water or oxygen molecules, respectively. In the third case, the free volume was filled by a mixture of water and oxygen with water content just over 50% by mole (Table 3). This was performed because it has been shown [21] that diffusion coefficients of small molecules in aqueous solutions of polymers are strongly dependent upon concentration if the system contains less than about 50% water, but are less sensitive to concentration if the water content is greater. Although it is clear that a variety of water/oxygen concentrations can exist in water based primers in real situations, in this preliminary study the mole fractions presented in Table 3 have been chosen to reduce the effects of concentration on diffusion rate.

It can be seen from Table 3 that the diffusion constants of

Table 3
Diffusion constants of water and oxygen in the simulated systems, ($\times 10^{-6}$ cm^2/s)

System	Molar fraction of water in water/oxygen systems (%)	Water		Oxygen	
		Pure water	Water/oxygen	Pure oxygen	Water/oxygen
P0 + 1158	58	4.62	4.47	3.32	2.17
P1 + 1158	60	4.13	1.13	3.35	0.43
P1 + 1172	54	2.13	0.9	4.00	0.8

water have the highest value in the fully crosslinked P0 + 1158 system and decrease with increasing amount of the free hydroxyl group concentration in partially crosslinked P1 + 1158 and P1 + 1172 systems. The trend is more pronounced in the mixed water/oxygen systems where the mobility of water was found to be generally lower than in the corresponding pure water systems. This result suggests that some water molecules become partially immobilised by hydrogen bonding with the unreacted hydroxyl groups of the resin and/or crosslinker molecules. The hydrogen bonds were also apparent via direct visualisation of the atomistic models.

To validate the simulated trends in the diffusivity of water, a series of experiments has been performed in order to estimate the water penetration rate in a saturated vapour chamber into the films of specially synthesised unpigmented materials identical to the ones simulated in this work. The predicted trends in the diffusivity for all studied materials have been confirmed experimentally via these indirect measurements [22].

The interpretation of the oxygen diffusion constants is less straightforward. In most cases, oxygen is slower than water (Table 3), which can be primarily attributed to the mass difference. However, in the P1 + 1172 system oxygen is more mobile than water, which is because in this system more water molecules could be immobilised by the hydrogen bonding with unreacted hydroxyls than in the other systems. In the mixed water/oxygen systems oxygen is less mobile than it is in the pure oxygen system, which can be expected for a gas in aqueous solution compared to the pure gas. In the P1 + 1158 and P1 + 1172 systems oxygen diffusivity dropped dramatically. In these systems the numerous hydrogen bonding between water and unreacted crosslinker hydroxyl groups can decrease diffusivity of the gas due to the reduction of free volume by immobilised water.

It can be concluded that oxygen diffusion is affected by the amount of water present in the system as well as by the number of specific interactions between water molecules and the polymer matrix.

4.4. Alumina/epoxy interface: strength and molecular mechanism of adhesion

The values of the work of adhesion calculated for the simulated systems using Eq. (2) are presented in Table 4 together with the number of free hydroxyl groups per unit surface area. It can be seen that there exists a correlation between the number of free hydroxyl groups available for hydrogen bonding and the strength of adhesion. It can therefore be suggested that adhesion is stronger in the P1 + 1172 system because there is more unreacted hydroxyls present in this system (Tables 1 and 4) available for the adhesive bonding. In addition, 1172 molecules are more mobile and can more easily reach the interface to form a hydrogen bond with alumina. The hydrogen bonds have been directly observed in the atomic structures of the simulated systems. These predictions have been confirmed experimentally [11] suggesting that the crosslinker is able to affect adhesion properties of primers. The simulation procedure developed and tested in this work can therefore be applied for screening adhesion properties of prospective primers.

5. Conclusions

(i) A computational procedure has been developed which allows trends in the adhesion and barrier properties of low molecular weight crosslinked polymer systems to be theoretically predicted.
(ii) Application of the procedure to the low molecular weight water based epoxy primer systems indicated better adhesion and barrier performance of the P1 epoxy resin crosslinked by CYMEL 1172 crosslinker which is in agreement with experimental observations.
(iii) The molecular mechanisms of adhesion of the primers to a metal oxide substrate as well as diffusivity of small molecules through the primers have been suggested.

Table 4
Relative difference in the work of adhesion in the simulated systems

System	Number of hydroxyls per unit surface area (Å^2) ($\times 10^2$)	Relative difference in work of adhesion (J/m^2)
P0 + 1158	4.6	0.11
P1 + 1158	3.6	0.0
P1 + 1172	5.2	0.67

(iv) The methodology can be applied for the 'prior to synthesis' estimation of properties of the prospective primer candidates as well as for any other crosslinked polymer systems of a relatively low molecular weight (however, in principle, the size of model systems is only limited by the available computer resources, not the algorithms).

(v) Although the work of adhesion and diffusion constants could only be indirectly compared to experimental measurements, qualitative trends predicted by the atomistic simulation procedure have been shown to be in agreement with experimental observations and can therefore be used as a guide for further research and synthesis.

Acknowledgements

Discussions with Prof. Kurt Kremer (Max-Planck Institut fűr Polymerforschung, Germany) were very helpful and are much appreciated.

References

[1] Yarovsky I. Aust J Phys 1997;50:407.
[2] Muller-Plathe E. J Chem Phys 1991;94:3192.
[3] Pant KPV, Boyd RH. Macromolecules 1992;25:494.
[4] Pant PVK, Boyd RH. Macromolecules 1993;26:67.
[5] Gee RH, Boyd RH. Polymer 1995;36:1435.
[6] Han J, Boyd RH. Polymer 1996;37:1797.
[7] Takeuchi H, Okazaki K. Mol Simul 1996;16:59.
[8] Fritz L, Hofmann D. Polymer 1997;38:1035.
[9] Bharadwaj RK, Boyd RH. Polymer 1999;40:4229.
[10] Hofmann D, Fritz L, Inbrich J, Paul D. Comput Theor Polym Sci 2000;10:419.
[11] Al Mubasher A. Evaluation of prepainted Zincalume coated with chromate-free pretreatment and primers after five years exposure at Bellambi Point, BHPR Report no. BHPR/SF/R/010, 1996 (confidential).
[12] Theodorou DN, Suter UW. Macromolecules 1985;18:1467.
[13] Polymer User Guide, Molecular Simulations Inc., San Diego, USA, 1996.
[14] Sun H, Mumby SJ, Maple JR, Hagler AT. J Am Chem Soc 1994;116:2978.
[15] Sun H, Mumby SJ, Hagler AT. J Phys Chem 1995;99:5873.
[16] Bicerano J. Prediction of polymer properties. 2nd ed. New York: Marcel Dekker, 1996. p. 403.
[17] Allen MP, Tildesley DJ. Computer simulation of liquids. Oxford: Clarendon Press, 1987.
[18] Choi K, Jo WH. Macromolecules 1995;28:8598.
[19] Dupre A. Theorie Mechanique de la Chaleur, Paris, 1869.
[20] Evans E, Burgar I. unpublished data, BHP Billiton Pty. Ltd.
[21] Eichinger BE, Rigby DR, Muir MH. Comput Polym Sci 1995;5:147.
[22] Peterson RH. Water Uptake of Clear Primers on ZINCALUME® (BHP Report BHPR/SF/N/035, 1996 (confidential).