

Atomistic modelling of interfacial bonding at metal/polymer interface

Marta M.D. Ramos^{*}, Judite P.P. Almeida

Departamento Física, Universidade do Minho, Largo do Paço, 4700-3200 Braga, Portugal

Abstract

The chemical bonding at a metal/polymer interface is believed to play an important role in adhesion. The interfacial bonding and consequently adhesion are influenced directly by the way in which the interface is formed. Atomistic modelling of interface formation has the potential to yield significant progress in the field of adhesion between metals and polymers. In order to study the nature of bond formation at metal/polymer interface, the authors have investigated the interaction of aluminium atoms with a trans-polyacetylene fragment. Self-consistent geometry optimization and molecular orbital calculations of adsorbate-substrate system have been carried out within CNDO approximation in a cluster model framework. The results suggest that aluminium dimer (Al_2) bound to a polymer chain is energetically favourable. The adhesion of aluminium dimers to polyacetylene is predicted to be somewhat weaker than that of isolated aluminium atoms to polyacetylene. The compound formation is accompanied by charge transfer between metal and polymer. As a result, charge rearrangement amongst polyacetylene atoms is induced. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Atomistic modelling; Adhesion; Polyacetylene; Interfaces

1. Introduction

Traditionally, polymers have been known for their flexibility and easy processing into coatings and films, but not for their electrical properties. Over the past decade, there has been considerable interest in the use of conjugated polymers as active components of electronic and optoelectronic devices. These polymers exhibit metal-type conductivities whilst retaining the physical and mechanical properties characteristic of polymer materials.

Further developments of electroluminescent, photoconductive and other optoelectronic devices [1–3] based on conducting polymers requires a better understanding of chemical interactions at metal-polymer interfaces and their consequences for adhesion. As in other areas, theoretical modelling can play an important role in understanding the basic physics of contact formation.

The softness of conjugated polymers leads to strong coupling between the polymers' electrons and lattice vibrations (phonons) [4]. Therefore, it is necessary to perform self-consistent calculations of electronic wave functions and atomic positions in order to study the interfacial properties.

The self-consistent molecular dynamics are essential, for the molecule distorts in a complex way which has a significant effect on the adhesion.

The geometrical simplicity of polyacetylene and the small size of its monomer makes it an ideal system to address these questions, which should also apply to other conjugated backbone polymers. Chemical bonding and charge transfer at the interface between aluminium and trans-polyacetylene (t-PA) have been studied using a quantum chemistry molecular dynamics method.

2. Theoretical methods

Molecular-dynamics computer simulations have been performed of an adsorbate-substrate system using interparticle forces evaluated from self-consistent electronic quantum-mechanical calculations. The electronic structure calculations were performed at the complete neglect of differential overlap (CNDO) level, using a linear combination of atomic orbitals and a cluster model framework. Metal and polymer chemistry is included within the self-consistent molecular dynamics. This approach is implemented in Harwell CHEMOS code [5–7].

In the calculations reported here, the CNDO parameters selected by Pople and Beveridge [8,9] have been used to give

^{*} Corresponding author. Tel.: +351-53-604-330; fax: +351-53-678-981
E-mail address: marta@fisica.uminho.pt (M.M.D. Ramos)

the best overall fit to minimal basis set ab initio Hartree–Fock calculations. No attempt has been made to re-parametrize in order to fit particular molecular properties. It should be noted that CNDO parameters are fixed in advance from a general approach, and are not regarded as adjustable parameters.

3. Results and discussion

3.1. The isolated t-PA chain

Before any chemical interaction of trans-polyacetylene (t-PA) with aluminium atoms is considered, a planar and finite chain of t-PA has been relaxed to equilibrium. The ground state geometry of a free-defect t-PA chain and a t-PA chain containing a positively charged soliton-type defect (which is one of the defects formed on doping [10]) were found, examining molecules of $t\text{-C}_{20}\text{H}_{22}$ and $t\text{-C}_{19}\text{H}_{21}^+$ as a model. The polyacetylene geometry predicted by CNDO compares well with the reported experimental data [11]. The dimerisation patterns in a t-PA chain with 20 carbon atoms is reported elsewhere [12].

3.2. Aluminium atoms on trans-polyacetylene

UPS studies of the deposition of aluminium on α,ω -diphenyltetradecaheptaene, a phenyl-capped model molecule for polyacetylene, indicate that aluminium atoms react pair-wise with the polyene part of the molecule. In order to study the interactions at the interface between aluminium and trans-polyacetylene the authors have considered the simultaneous reaction of two metal atoms with each t-PA molecule, in accordance with low coverage experiments. The aluminization of t-PA was modelled in the following way. Two aluminium atoms were brought close to the polymer, whilst the t-PA atoms were kept frozen. When the equilibrium was reached for metal atoms, the entire system was allowed to relax.

The adsorption of two aluminium atoms on t-PA either isolated or as dimers gives a local energy minimum, both bonding positions being stable. The aluminium dimers (Al_2) bound to a single trans-polyacetylene chain was found to be energetically more favourable. The present results suggest that the most stable position for the aluminium dimer is out of the molecular plane and with the aluminium atoms midway between the carbon–carbon bonds, rather than directly over the carbon atoms.

Aluminium is found to interact strongly with the trans-polyacetylene chain, leading to the formation of a metal–polymer bond. This type of interaction strongly modifies the geometrical structure of the polymer chain and induces the generation of new electronic states in one-electron band structure of the polymer. The structural relaxation of the trans-polyacetylene chain around the adsorption position creates a polaron type defect for aluminium dimer

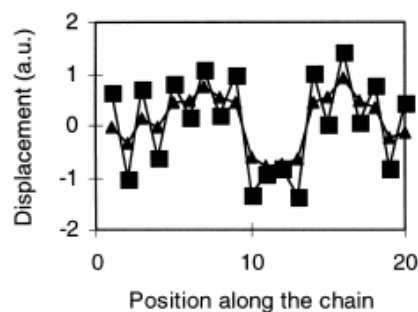


Fig. 1. Carbon (Δ) and hydrogen (\square) displacements out of the molecular plane caused by an aluminium dimer (Al_2) bound to a single free-defect t-PA chain: the marks indicate the data points that were calculated explicitly, the curves are simply a guide to the eye.

bonding, a soliton pair defect being formed otherwise. Detailed information about defect nomenclature and properties in conjugated polymers is given by Fisher et al. [4,7]. The chemical interaction between aluminium and trans-polyacetylene leads to a distortion of the molecular fragment both parallel and perpendicular to the molecular plane. The resulting atomic displacements perpendicular to the molecular plane are shown in Figs. 1 and 2. Molecular distortion was also predicted for insulating polyimide deposited on Al(100) surface [9,13].

3.3. Adhesion energy

Adhesion energies for the adsorption of aluminium dimers and isolated aluminium atoms on trans-polyacetylene are given in Table 1. These results show two main

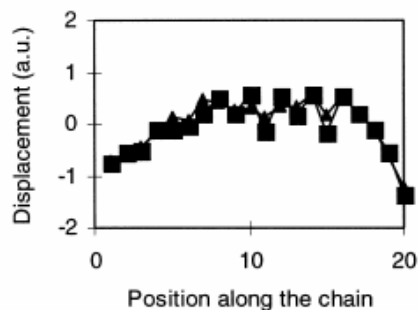


Fig. 2. Carbon (triangle) and hydrogen (square) displacements out of the molecular plane caused by two isolated aluminium atoms bound to a single free-defect t-PA chain: the curves are simply a guide to the eye.

Table 1
Adhesion energy of aluminium adsorbed on free-defect t-PA chain ($t\text{-C}_{20}\text{H}_{22}$) and a t-PA chain with a positively charged soliton ($t\text{-C}_{19}\text{H}_{21}^+$).

| Molecule | Adhesion energy ($\text{eV}/\text{\AA}^2$) | |
|----------------------------------|--|-------------------|
| | Aluminium dimer (Al_2) | Isolated Al atoms |
| $t\text{-C}_{20}\text{H}_{22}$ | 0.37 | 1.06 |
| $t\text{-C}_{19}\text{H}_{21}^+$ | 0.35 | 1.09 |

features. First, the adhesion energy of aluminium dimers to trans-polyacetylene is lower than the adhesion energy for the adsorption of isolated aluminium atoms. Second, the authors' results suggest that the magnitude of adhesion energy does not depend on polymer doping. The present earlier work [9,13] for insulating polyimide gave adhesion energies of polyimide to aluminium surface much lower than those obtained for adhesion of isolated aluminium atoms on polyimide.

Preliminary calculations using Pople and Beveridge parameters suggest serious overestimation of the magnitudes of binding energies. Some improvement can be achieved by using CNDO parameters determined by calibration with experimental data, since it will allow one to take account of interactions neglected by Hartree-Fock theory (e.g. correlation terms). Since the adhesion energies are strongly dependent on the CNDO parameter set used, the absolute value of calculated adhesion energies may not be correct. However, the predicted trends for adsorption positions are expected to be reliable.

3.4. Aluminium-induced charge transfer

The charge transfer to aluminium due to the interaction of two aluminium atoms with trans-polyacetylene is given in Table 2.

Charge transfer from aluminium to trans-polyacetylene (with and without a soliton-type defect) is predicted for the adsorption of two isolated aluminium atoms, whilst charge transfer in the opposite direction is predicted for an aluminium dimer bound to a single t-PA fragment. When polyacetylene is put into contact with metal atoms, a number of electrons flows from or to polyacetylene, shifting one-orbital energies until the Fermi level of both materials is in coincidence [14]. The direction of electron transfer predicted is in accordance with the relative Fermi levels, which are given by the arithmetic average of electron affinity and ionization potential of N-electron ground state [12,15].

The compound formation induces charge rearrangements among the trans-polyacetylene atoms. Despite the presence of a conjugated system, charge rearrangement is induced not far from the reaction site when Al_2 -polyacetylene complex is formed. In contrast to dimer formation, the adsorption of two isolated aluminium atoms on polyacetylene leads to larger charge delocalization. In both cases it is clear that approximately 30% of the charge transfer to t-PA is actually stored on hydrogen atoms rather than the entire charge resting on carbon atoms. The changes in atomic charge of t-PA due to

Table 2
Charge stored in two aluminium atoms adsorbed on t-PA chain

| Molecule | Charge (electrons) | |
|---------------------|----------------------------|-------------------|
| | Aluminium dimer (Al_2) | Isolated Al atoms |
| t- $C_{20}H_{22}$ | -0.36 | +0.39 |
| t- $C_{19}H_{21}^+$ | -0.14 | +1.01 |

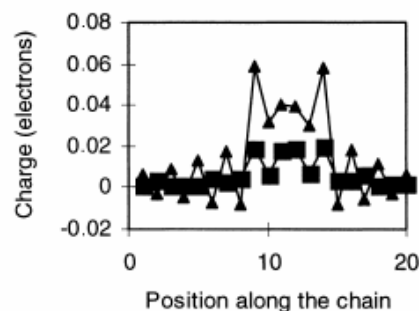


Fig. 3. Changes in atomic charges for carbon (Δ) and hydrogen (\square) atoms of t-PA caused by an aluminium dimer (Al_2) bound to a single free-defect trans-polyacetylene chain: the curves are simply a guide to the eye.

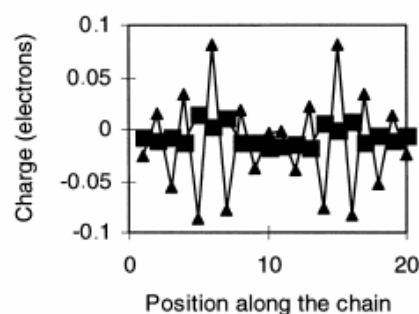


Fig. 4. Changes in atomic charges for carbon (Δ) and hydrogen (\square) atoms of t-PA caused by two isolated aluminium atoms bound to a single free-defect t-PA chain: the marks indicate the data points that were calculated explicitly, whilst the curves are simply a guide to the eye.

the chemical interaction of two aluminium atoms with a free-defect t-PA chain are shown in Figs. 3 and 4. For insulating polyimide intramolecular charge distribution was also found, with little charge transfer between metal and polymer [9].

4. Conclusions

In this work the authors have studied the interfacial properties of aluminium-polyacetylene such as chemical bonding and charge transfer, and assessed the consequences for adhesion. The results suggest that at low aluminium coverage the formation of Al_2 -polyacetylene complex is energetically favourable. Moreover, the metal induces charge rearrangements among the polymer atoms. The adhesion of aluminium dimers to trans-polyacetylene is predicted to be somewhat weaker than that of isolated aluminium atoms. The experimental observation of the fracture surface within polymers suggests that adhesion might be related to the number of bonds needed to be broken in fracture process rather than the formation of strong metal-polymer bonds.

Acknowledgements

This work was supported in part by FEDER and PRAXIS XXI under project No. PRAXIS/2/2.1/FIS/26/94 and by JNICT under project No. PBIC/C/FIS/2151/95.

References

- [1] D.S. Soane, Z. Martynenko, *Polymers in Electronics: Fundamentals and Applications*, Elsevier, Amsterdam, 1989.
- [2] E. Ruiz-Hitzky, *Adv. Mater.* 5 (1993) 334.
- [3] M.S. Weaver et al., *Thin Solid Films* 273 (1996) 39.
- [4] A. Fisher, W. Hayes, D.S. Wallace, *J. Phys.: Condens. Matter* 1 (1989) 5567.
- [5] D.S. Wallace, D. Phil. Thesis, University of Oxford, 1989.
- [6] D.S. Wallace et al., *J. Phys.: Condens. Matter* 3 (1991) 3879.
- [7] D.S. Wallace et al., *J. Phys.: Condens. Matter* 3 (1991) 3905.
- [8] J.A. Pople, D.L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970.
- [9] M.M.D. Ramos, A.M. Stoneham, A.P. Sutton, *Acta Metall. Mater.* 41 (1993) 2105.
- [10] A.N. Chuvyrov, G.I. Yusupova, *JETP Lett.* 50 (1989) 420.
- [11] C.S. Yannoni, T.C. Clarke, *Phys. Rev. Lett.* 51 (1983) 1191.
- [12] M.M.D. Ramos, A.M. Stoneham, A.P. Sutton, *Synthetic Metals* 67 (1994) 137.
- [13] M.M.D. Ramos, A.M. Stoneham, A.P. Sutton, *Phil. Mag.* A67 (1993) 797.
- [14] W.J. Brennan et al., *J. Phys. D: Appl. Phys.* 28 (1995) 2349.
- [15] A.M. Stoneham, M.M.D. Ramos, *J. Sol. State Chem.* 106 (1993) 2.