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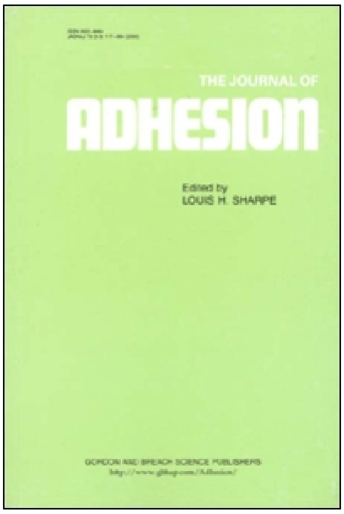

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
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Lieng-Huang Lee[a]
[a] Webster Research Center, Xerox Corporation, Webster, New York, USA

To cite this Article Lee, Lieng-Huang(1994) 'Molecular Bonding and Adhesion at Polymer-Metal Interphases', The Journal of Adhesion, 46: 1, 15 — 38
To link to this Article: DOI: 10.1080/00218469408026646
URL: http://dx.doi.org/10.1080/00218469408026646

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J. Adhesion, 1994, Vol. 46, pp. 15–38
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Molecular Bonding and Adhesion at Polymer–Metal Interphases*

LIENG-HUANG LEE

*M/S 114-39A, Webster Research Center, Xerox Corporation, Webster, New York 14580, USA***

(Received January 21, 1993; in final form August 28, 1993)

The purpose of this review is to demonstrate that there are well established molecular bonding and strong interactions between monomers or polymers and metals. We discuss both theoretical and experimental work related to adsorption and adhesion at polymer-metal interphases. Firstly, we briefly describe the fractal nature of polymer-metal interphases, and the effect of chemisorption on fractal dimension. Secondly, we mention several theoretical studies related to the models and the conformation of polymer segments to metal surfaces. Recent theoretical work by others with molecular modeling has provided some insight about the interfaces; however, this type of work is still at an early stage. Thirdly, we cite the experimental work by others with XPS, SERS (surface-enhanced Raman scattering spectroscopy), Mössbauer emission spectroscopy, etc., on chemisorption, molecular bonding, redox interaction, restructuring of polar groups, and contact oxidation of polymers on metal surfaces. Among them, SERS and XPS are capable of describing chemical composition and conformation right at the interfaces. These results appear very valuable in understanding the formation of the architectural framework of a functional interphase beyond the superficial blending. In general, some preliminary data indicate that adhesion of polymers is greatly improved by various forms of strong interactions, *e.g.*, chemisorption and molecular bonding at polymer-metal interphases. However, strong chemical reactions at the interphases may not be always beneficial to adhesion and physical properties.

KEY WORDS acid; adhesion; adsorption; base; bonding; chemisorption; conformation; dicyandiamide; contact; epoxy; fractal; grafting; interaction; interface; interphase; metal; molecular; oxidation; polymer; redox; restructuring.

INTRODUCTION

A sharp interface is the boundary between two phases, while a polymeric interphase, first described by Sharpe,[1] is a transition zone between the surface of a substrate and the bulk of a polymer that is cured or solidified against the substrate. Thus, an interphase is a region with finite volume and a distinct physical gradient in properties.[2] If either homogeneous phase influences a region of the other phase in a manner such as its chemical

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*Presented at the International Symposium on "The Interphase" at the Sixteenth Annual Meeting of The Adhesion Society, Inc., Williamsburg, Virginia, U.S.A., February 21–26, 1993.

**New address: 796 John Glenn Blvd., Webster, New York 14580, USA.

and physical structures, then this region of the modified material can also be termed an interphase or an interfacial zone.[3] For this unique interphase, there are interfaces adjacent to each homogeneous phase. Thus, in the literature, the definition of interphase varies, and the boundary of interphases is somewhat indefinite. Despite the lack of clear definition, we attempt to gain some insight from this review about the role of strong interactions at polymer-metal interphases. Strong interactions originate from chemisorption, and chemisorption eventually leads to molecular bonding, which is in between weak physical interactions and chemical reactions. In some instances, molecular bonding may result in chemical reactions.

First, we briefly describe the fractal nature of polymer-metal interphases. We shall mention that even fractals are affected by chemisorption. Then we discuss chemisorption of monomers and polymers alongside the resultant molecular bonding. Recent work on interactions of polymer segments with metal surfaces is in the budding stage. The theoretical aspects are based on the Hartree-Fock molecular orbital (HFMO) method and the density functional theory (DFT). On the other hand, the experimental aspects are chiefly based on XPS, surface enhanced Raman scattering spectroscopy (SERS), and Mössbauer emission spectroscopy. We shall mention some of these new approaches in the establishing of molecular bonding and adhesion at polymer-metal interphases.

FRACTAL NATURE OF POLYMER-METAL INTERPHASES

Most polymer-metal interfaces are fractal in nature. The boundaries are generally not smooth microscopically. If the interface is formed through diffusion, the diffusion front can be simulated by computer calculations[4] showing a polymer interface (Figure 1) and the connected region of a silver/polymer interface (Figure 2), which is produced by depositing silver electrochemically onto a polyimide film.

The adsorption of polymers[5] on fractal surfaces has been reported recently. The amount of a polymer, m, physically adsorbed under plateau (monolayer) conditions is a

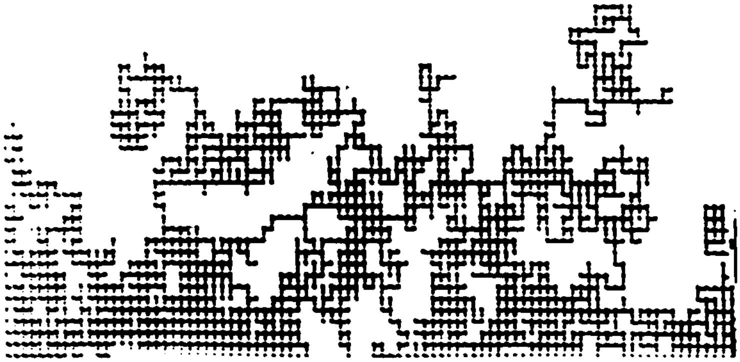


FIGURE 1 Fractal nature of polymer interface (computer generated), reprinted with permission from R. P. Wool, in *Fundamentals of Adhesion*, L. H. Lee, Ed. (Plenum Press, New York, 1991), p. 207.

FIGURE 2 Fractal nature of metal interface (computer generated), reprinted with permission from R. P. Wool, in *Fundamentals of Adhesion*, L. H. Lee, Ed. (Plenum Press, New York, 1991), p. 207.

function of the molecular weight[5] M_w

$$m \propto M_w^{-\beta} \tag{1}$$

where β is a coefficient containing information on two geometries involved in the process: the surface geometry and the distorted geometry, which the polymer molecule assumes upon adsorption. Thus, β may be expressed as

$$\beta \simeq D_a v_{ap} \tag{2}$$

where D_a is the fractal dimension of the surface available for adsorption, and v_{ap} is a Flory-type exponent which reflects the mass distribution within the polymer molecule, adsorbed horizontally on the surface, at a certain distance from the surface where an effective horizontal radius, r_a, can be defined[6]:

$$r_a \propto M_w^{v_{ap}} \tag{3}$$

For most cases where the conformers' envelope of the polymer is oblique, $v_{ap} = D_{ap}^{-1}$, where D_{ap} represents the mass-fractal dimension of the polymer molecule, horizontal to the surface. For most polymers, $\beta \simeq 0.8$. For the adsorption of polystyrene ($M_w \sim 67-1820 \times 10^3$) on aluminum from cyclohexane at 34°C, $\beta \simeq 0.87 \pm 0.02$. If the surface is an oxide, *e.g.*, alumina, the β value is much higher, *e.g.*, 1.41 ± 0.07 under the same condition.

Surface fractal dimensions[7] for metals are between 2.0 and 2.7. On the other hand, those for oxides, *e.g.*, alumina, are considerably higher, *e.g.*, 3.0. Thus, it is important to distinguish whether the bulk phase is a metal or a metal oxide, and especially how the oxide is formed. The topography of the oxide layer can further affect the fractal dimension.

If a chemical or molecular interaction enters the surface/molecule complex, the selectivity of adsorption is not only dictated by geometric accessibility but also by chemical heterogeneity of the surface. Then, the chemisorptive capacity (or the amount) of polymer particles (or molecule)[5], m_c, may be expressed as

$$m_c \propto R^{D_c} \tag{4}$$

where D_c is the fractal dimension related to chemisorption, and R is the radius of the particles. For the majority of metallic catalysts, D_c values have been determined to be in the range of 1.7 and 2.3. It is important to note that D_c is a characteristic exponent for a given molecule/surface pair, and not necessarily of the material itself.

INTERACTIONS OF METAL ATOMS WITH POLYMER SURFACES

In a review, Ho *et al.*[8] have examined the interactions of metal atoms with polymer surfaces. The studies on the deposition of various metal atoms on the pyromellitic dianhydride-oxydianiline (PMDA-ODA) polyimides, as carried out chiefly by IBM researchers, were described. The experimental aspects in using XPS for the study of systems has been reviewed by di Nardo.[9] The application of the Hartree-Fock molecular orbital (HFMO) method has been reported by Chakraborty *et al.*[10] for the acrylic polymers. They used the MNDO method to obtain the minimum structures for the model compound/aluminum complexes with respect to important geometric degrees of freedom. From the interactions of dimers of PMMA, they found that aluminum atoms interact primarily with the carbonyl group, and to a lesser extent with the methoxy functionality. This trend is also true in the case of polyacrylic acid, PAA. Chakraborty[11] illustrated the interaction (Figure 3) that electrons are transferred from the HOMO of the polymer to the LUMO (or the conduction band edge) of the metal atom, or from the HOMO (or the valence band edge) of the metal atom to the LUMO of the polymer. This interaction is commonly known as one type of molecular interaction or the acid-base interaction.

We have previously discussed[12, 13] molecular interactions between discrete molecules and between a discrete molecule and a surface. For discrete molecules, besides dispersion, there are at least five major interactions: electrostatic, polarization, charge transfer, exchange repulsion, and the coupling (or mixing) of any of the four interactions. On the other hand, between a discrete molecule and a metal surface,[12,13] there is one additional interaction due to the internal transition of electrons between the bulk and surface of the metal.

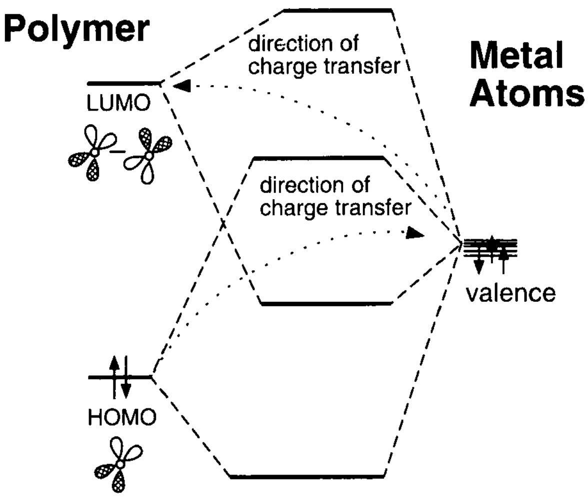


FIGURE 3 Interaction between metal atoms and polymer, reprinted with permission from A. K. Chakraborty, *et al.*, *J. Polym. Sci. A. Polym. Chem.* **28**, 3185 (1990).

We have pointed out previously[14] that for the acid-base interaction, we need to differentiate between hard and soft species according to their energy gaps between the HOMO and LUMO of frontier orbitals. The interaction is governed by the HSAB principle,[15] stating that hard acids prefer to interact with hard bases, and soft acids with soft bases.

Furthermore, in order to obtain an optimum adhesive energy, it is important to achieve an optimum distance because the adhesive energy has been established by Ferrante *et al.*[16,17] to be a universal function of the intermolecular distance. For an acid-base interaction,[18] the intermolecular distance should be below 4 Å. Thus, it is necessary for polymer segments to conform to the metal surface to achieve this optimum distance.

In general, the theoretical calculations for metal atoms adsorbed on polymer surfaces based on the HFMO have been confirmed by experimental work, such as High Resolution Electron Energy Loss Spectroscopy (HREELS).[19] A brief mention of these works on metal-polymer interactions will lead to the following discussions about different interactions between polymer and metal or oxide surfaces.

MOLECULAR BONDING OF ORGANIC FUNCTIONAL GROUPS AND MONOMERS ON METAL SURFACES

Before we examine interactions at polymer-metal interphases, let us discuss several simple examples of chemisorption of organic functional groups and monomers on metal surfaces. Rodriguez[20] studied the bonding of acetate (CH_3COO), methoxy (CH_3O), thiomethoxy (CH_3S), and pyridine (C_6H_5N) to the Cu surface by employing semi-empirical MO-SCF calculations (INDO/S) and metal clusters of limited size (Cu_n, where $n = 16$ or 18 atoms). The functional groups, CH_3COO, CH_3O, and CH_3S, react as bases (electron donors) when chemisorbed on the Cu surface. For these species, the chemisorbed bond is dominated by the interaction between the LUMO of the adsorbate and the Cu(4s, 4p) bands. The relatively-weak C—S bond is CH_3S_a, which decomposes into S adatoms and alkanes through a very exothermic process. On the other hand, the decompositions of CH_3O_a are almost thermoneutral and yield H_2CO and H_a species.

The bonding mechanism of pyridine to Cu involves a large charge transfer into Cu (4s, 4p) orbitals, and a very small electron transfer from the substrate into the C-N antibonding orbital of the adsorbate (π-backbonding). Since Cu is poor at π-backdonation, the metal is inactive toward the pyridine decomposition.

A similar calculation[21] has been carried out for the adsorption of OH, SH, and CH_3 on silver. The functional groups OH and SH appear as net electron acceptors (σ-donors and π-acceptors) when adsorbed on a-top and bridge sites of the Ag(100) and the Ag(111) faces. Bonding mechanisms of OH and SH involve transfer of electrons from the highest occupied σ-MO of the adsorbate (3σ orbital in OH and 5σ in SH) toward the surface, and charge transfer from the substrate into the lowest empty π-MO of the admolecule (π-orbital in OH and 2π in SH). The bond of methyl to the Ag surface is controlled by the weak interaction between the $CH_3(3_{a1})$ orbital and the Ag(5s, 5p) orbitals.

Recently, the effect of temperature on the reaction of acrolein with the Ag surface has been studied with SERS by Fujii *et al.*[22] At 120 K, acrolein is physisorbed on the Ag surface, and the physisorbed film can be desorbed at 150 K. However, at 180 K, the main adsorbate has a C=O bond chemisorbed to the Ag surface (Type A) (Figure 4).

On heating to 240 K, Type A species is converted to Type B configuration in which acrolein lies flat on the Ag surface with both the C=O and C=C bonds coordinated (or chemisorbed) to the Ag surface. During the successive temperature change, a third adsorption state (Type C) (Figure 5) is shown to be Ag(I) acrylate, indicating that an oxidation has taken place at the surface, presumably catalyzed by Ag. The adsorbate assumes an end-on structure with the symmetry axis of the carboxy group perpendicular to the surface. After the temperature is increased from 180 to 240 K, the adsorbed acetate ion shows a reversible tilting of the symmetry axis. This reversible orientation change also occurs for the Ag acrylate (Type C) adsorbed on the cold-evaporated Ag film. The above structure variations demonstrate the dynamic nature of the interface when the temperature is changed, and a molecular interaction in the form of physisorption can be transformed into a chemical reaction.

One interesting example of monomer-metal interactions is electrochemical grafting on the metal surface. Boiziau and Lécayon[23,24] have investigated the grafting of acrylonitrile to the Ni surface (Figure 6). For the initial contact, the acid-base reaction[25] has been shown to be highly probable between nickel and acrylonitrile. Following the initial contact, the polymerization proceeds from the grafted sites (Figure 7). In this case, the interphase consists of mainly polyacrylonitrile and nickel. A similar grafting of 2-methyl-propenenitrile on Ni has been also reported by Deniau *et al.*[26]

A thin insulating film of poly (N-vinyl-2-pyrrolidone)[27] can be produced on the surface of a Pt electrode. The grafted polymerization (Figure 8) is initiated in a manner similar to the grafting of acrylonitrile on the Ni surface. Generally, these mechanisms are possible if the substituent is an electron-donating group capable of accommodating the cations formed by the reaction of the ethylenic double bond with an electron-deficient site (or LUMO). On the other hand, nitrogen, oxygen, and the terminal carbon of the vinylic moiety, $CH_2=CH-$ are nucleophilic sites (HOMO).

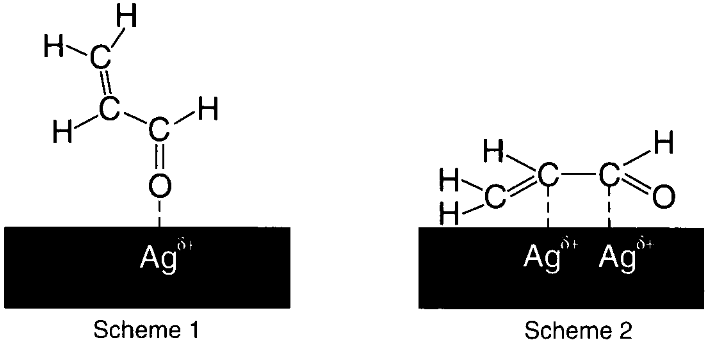


FIGURE 4 SERS study of chemisorption of acrolein on the silver surface, reprinted with permission from Fujii *et al.*, *Surf. Sci.* **277**, 220 (1992).

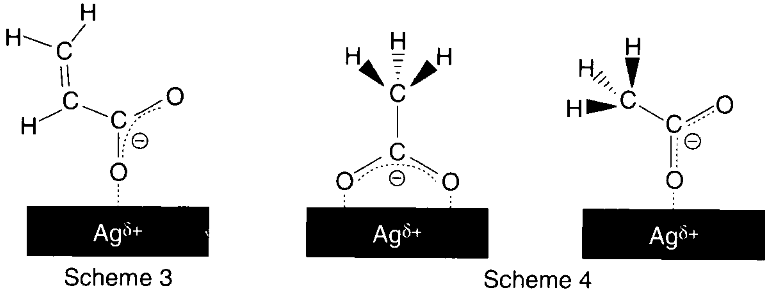


FIGURE 5 SERS study of the oxidation of acrolein into acrylates on the silver surface, reprinted with permission from Fujii *et al.*, *Surf. Sci.* **277**, 220 (1992).

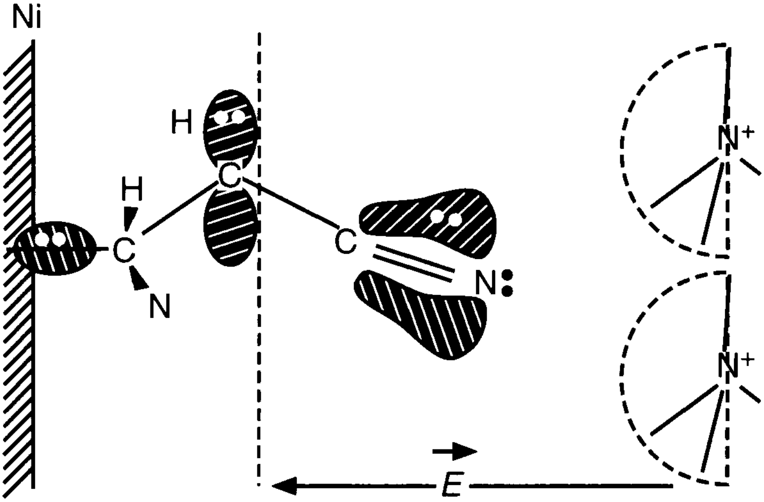


FIGURE 6 Chemisorption of acrylonitrile to the nickel surface, reprinted with permission from C. Boiziau and G. Lécayon, *Int. J. Adhes. Adhes.* **6** (4), 207 (1986).

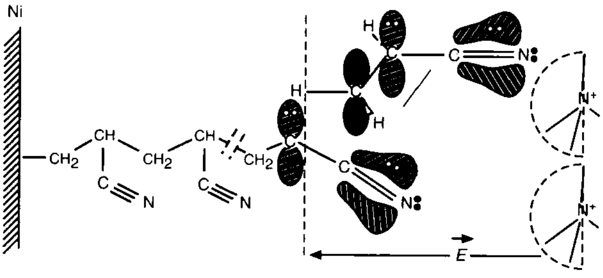
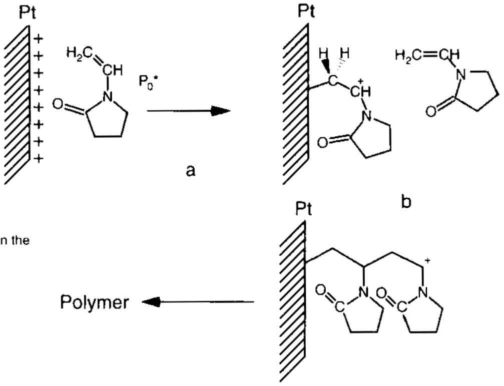


FIGURE 7 Graft polymerization of acrylonitrile on the nickel surface, reprinted with permission from C. Boiziau and G. Lécayon, *Int. J. Adhes. Adhes.* **6** (4), 207 (1986).



* (The molecule is represented in the synperiplanar form.)

FIGURE 8 Electroinitiated chemisorption and polymerization of N-vinyl-2-pyrrolidone on the platinum surface under anodic polarization (the molecule is represented in the synperiplanar form), reprinted with permission from E. Léonard-Stibbe *et al.*, in *Polymer-Solid Interfaces* (Institute of Physics, UK, 1992), p. 93.

In the case of metal oxides, a theoretical study on the basis of the acid-base interaction carried out by Holubka *et al.*[28] has shown the difference between an acrylate ester and a methacrylate ester in the interaction with aluminum oxide (Figure 9). Complete geometrical optimization is carried out using the MNDO semi-empirical method. Though most metals are Lewis bases, aluminum can also be treated as a Lewis acid (and the oxygens, correspondingly, as Lewis bases). For the proposed model, the calculated Al—O bond distance of 1.73 Å is in close agreement with the published value of 1.785 Å. The bonding process would result in the formation of intermediates as shown in Structure (a) (Figure 9). The next highest unoccupied MO for each monomer would suggest the reaction through the carbon oxygen. Interactions of these orbitals with aluminum oxide would result in Structure (b) (Figure 9). Thus, the acrylic unsaturation interacts more strongly with aluminum oxide in the form of a dimer than does the methacrylate unsaturation.

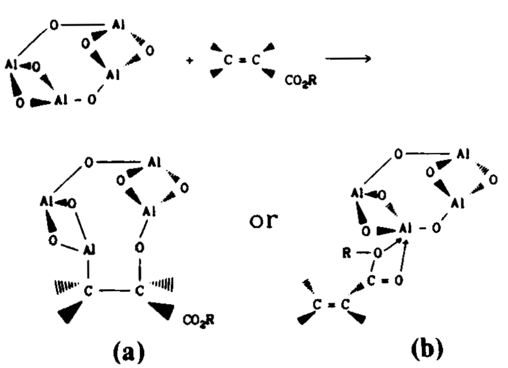


FIGURE 9 Interactions between aluminum oxide and acrylate and methacrylate esters, reprinted with permission from J. Holubka *et al.*, *J. Adhes. Sci. Technol.* **6**, 243 (1992).

MODELS FOR POLYMER-METAL SURFACE INTERACTIONS

Density Functional Formalism

In general, the interactions of a polymer with a metal surface differ from the chemisorption of small molecules on a metal surface. For small organic molecules or metal atoms, the energy is dominated by that of high-density core electrons, and there is no need to consider the competition between rotational conformation energies and binding energies associated with specific functional groups. Thus, the first type of quantum mechanical calculation based on the Hartree-Fock molecular orbital (HFMO) method is quite adequate. Shaffer *et al.*[29,30] demonstrated that the rotational conformation statistics of adsorbed PMMA molecules is quite different from that observed in the bulk. In contrast, metal surfaces have a large number of low-density electrons that constitute the valence band. Hence, the HFMO theory without configuration interaction is not appropriate for calculating interactions of small molecules with metal surfaces.

In contrast, the second type of quantum mechanical calculation involves the energy of hypersurfaces characterizing the polymer segment-surface interactions. This approach using the density functional theory (DFT) method is more suitable in solving the many-electron problem. DFT is based on the concept that electronic properties can be described by electron density instead of wave functions (or probability amplitudes) alone. Shaffer and Chakraborty[29,31] extended their earlier work on the interactions between metal atoms and polymers to those between PMMA oligomers and the aluminum surface. Chakraborty[11] has shown that the latter interactions are more complicated, partly because simple potentials cannot represent the enthalpic part of the interactions and partly because electronic properties of the surface affected by organic molecules have to be taken into account. Thus, the DFT of the inhomogeneous electron gas is used to compute interaction energies (or energy hypersurfaces) for the PMMA-aluminum system.

According to the Hohenberg-Kohn theorem,[32] the ground state energy of a many-electron system is a unique function of the electron density distribution, $n(\mathbf{r})$. The energy function may be expressed as:

$$E[n(\mathbf{r})] = \int V^{ex}(\mathbf{r})\, n(\mathbf{r}) d\mathbf{r} + \frac{1}{2}\iint \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' + G[n(\mathbf{r})], \tag{5}$$

where $\mathbf{r}$ and $\mathbf{r}'$ are spatial coordinates; the first term is the electrostatic interaction of the external potential, $V^{ex}(\mathbf{r})$, with the electron density; the second term denotes the electron-electron repulsion; and the third term, $G\,[n(\mathbf{r})]$, is a unique electron density distribution function, which can be separated into two terms:

$$G[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})], \tag{6}$$

where $T_s[n(\mathbf{r})]$ is the kinetic energy of a noninteracting electronic system with a density of $n(\mathbf{r})$, and $E_{xc}[n(\mathbf{r})]$ is the exchange energy associated with many-body Fermi and Coulomb correlations. It should be noted that $V^{ex}(\mathbf{r})$ is negative for electrons in the field of a nuclear charge density.

A term, Lagrange multiplier, μ, or chemical potential, can be expressed as the Lagrange-Euler's equation:

$$\mu = V^{ex}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + \frac{\delta T_s[n(\mathbf{r})]}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \tag{7}$$

If $T_s[n(\mathbf{r})]$ and $E_{xc}[n(\mathbf{r})]$ are known, the chemical potential can be solved by the above equation. Since the general expressions for these two terms do not exist for systems with an inhomogeneous electron density distribution, one has to rely on approximation. These complicated approximation methods have been discussed in Ref. 30 and will not be elaborated upon here. Current efforts in studying the nature of segment level interactions at polymer-metal interfaces are based on performing quantitatively accurate Kohn-Sham calculations. In order to perform these first-principle calculations, a model of the metal surface must be chosen.

Models of Metal Surfaces

There are at least three types of models:[32,33] 1) the jellium model for the s-p bonded metals; 2) the cluster model, especially for transition metals; and 3) the slab model. In a simple jellium model,[11] the detailed potential experienced by the electrons affected by the ions located at lattice sites is smeared in terms of a uniform positive charge background that terminates abruptly at the sharp interface. The delocalized valence electrons move in the field of the smoothed-out potential generated by the uniform positive background charge density. The functional form of that density is given by

$$\rho_o^{ex}(z) = \begin{cases} \rho, & z < 0 \\ 0, & z > 0 \end{cases} \tag{8}$$

where z is the coordinate normal to the surface, and ρ is the average density of valence electrons in the bulk metal.

In Figure 10, the positive background and the electron densities for two different bulk densities are plotted *versus* the distance (or Fermi wavelength). The bulk charge density is related to the Winger-Seitz radius, r_s, of the metal by

$$\rho = (4/3 \cdot \pi r_s^3)^{-1} \tag{9}$$

Values of r_s for typical metals range between 1.5 and 6 bohr, and that for aluminum is 2.07 bohr.

The jellium model reproduces many properties of simple metals very well.[11,34,35] For more accurate calculations of aluminum and transition metals, the surface has also been modeled as a finite cluster of metal atoms. The size of the cluster is selected to match the cohesive energy and Fermi level of the metal. For aluminum, roughly 40 atoms should be adequate for the calculations; however, 61 atoms have been measured with a novel position-sensitive, time-of-flight mass spectrometer.[36] After the model of the metal is selected, one can proceed to calculate the polymer segmentmetal surface interaction with the DFT.[11]

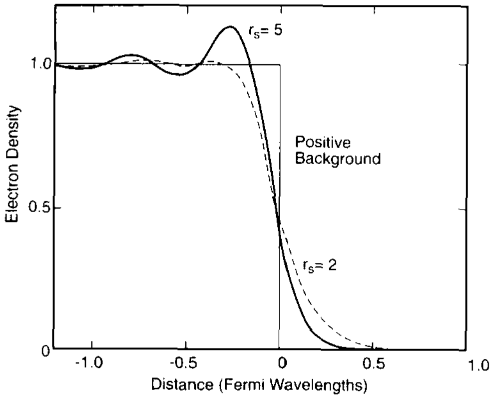


FIGURE 10 Electron density in surface region of uniform-background jellium model for metal; one Fermi wavelength is equal to $2\pi/k_F$. Reprinted with permission from N. D. Lang, *Solid State Commun.* 7, 1047(1969).

Model for the Polymer

Shaffer *et al.*[30] used PMMA oligomers as the model compounds and the charge density distribution is $\rho_p^{ex}(\mathbf{r})$ (ex: external potential). The charge denstiy around the ith atom, $\rho_i^{ex}(\mathbf{r})$, becomes:

$$\rho_i^{ex}(\mathbf{r}) = \frac{8(\chi_i - Z_i)}{\pi \xi_i^3} \exp\left(-\frac{4}{\xi_i}(\mathbf{r} - \mathbf{r}_i) \right) \tag{10}$$

where $\mathbf{r}$ is the spatial coordinate; ξ_i is the van der Waals radius for atom i; χ_i is the total electron count for each atom; Z_i is the atomic number; and $\mathbf{r}_i$ is the location of the ith nucleus. The pre-exponential constant is determined by the normalization condition that requires that the net electron density around atom i equals the difference between the total electron count and the total positive nuclear charge. The total charge density for the polymer model compound is then constructed as the sum over the charge densities centered at each nucleus.

$$\rho_p^{ex}(\mathbf{r}) = \sum_{i=1}^{M} \rho_i^{ex}(\mathbf{r}) \tag{11}$$

where the sum runs over the M nuclei in the molecule.

As a result of conformation, polymer segments tend to adsorb on the metal surfaces through various functional groups. The location and orientation of the monomer unit is described by the distance of a reference atom from the surface and the Eulerian angles. Various internal degrees of freedom, such as the torsion angle, are discussed in Ref. 30. The energetics for the interaction of PMMA monomers with an aluminum surface depend strongly on the orientation in which the monomer approaches the surface. There are two strongly-interacting functional groups per segment in PMMA, the methoxy group and the carbonyl group. Shaffer *et al.*[30] have explored the energy hypersurfaces in some detail and provided an empirical force field that can be used for simulating the interfacial chain structure.

Interfacial Dynamics of Polymer Segments on Metal Surfaces

There have not been many studies on the interaction of polymer segments with metal surfaces. Shaffer *et al.*[30] have recently investigated the segment level interactions between PMMA and aluminum surfaces. Besides the use of jellium model, they have used the Green function technique to calculate the interaction energetics as a function of internal and external degrees of freedom. However, these results are semiquantitative at best. Shaffer and Chakraborty[29] have solved the Kohn-Sham equations for the interactions between organic segments and large clusters of aluminum atoms. The calculations agree well with the jellium model.

Chakraborty *et al.*[31] have theorized that the interfacial chains adsorb in frozen-in, non-equilibrium conformations. Thus, the adsorbed polymer layer may be considered to be glass-like and history-dependent. Furthermore, the formation of the strong interacting polymer segments may result in high adhesive strength to the metal surface. Chakraborty and Adriani[37] have proposed a simple stochastic model to explain the dynamic conformation process. The rates of adsorption and desorption of individual sticker segments are strongly dependent on the state of neighboring segments. Hence, the chain relaxation is a cooperative process. The constaints, f, are a function of the steric factor, α, due to chain connectivity, the rotational conformations, β, on the surface and the entropic factor, γ, associated with the shortening of loops and tails upon the adsorption of a given sticker. In fact, the confirmation dynamics are similar to the kinetic Ising model, and the relaxation behavior is analogous to that of a glass-forming liquid. At low temperatures, these non-equilibrium structures do not relax to equilibrium within the experimental time-scale. On the other hand, at high temperatures, the relaxation dynamics is highly cooperative.[31]

Models of Interaction Energies

We shall briefly describe a typical interaction energy for a polymer segment or a model monomer adsorbing on a metal surface. With the models for the aluminum surface and the PMMA oligomers, Chakraborty *et al.*[31] developed a promising model for the calculation of interaction energies. The organic polumer is treated as a perturbation to the jellium surface and a linear response analysis is constructed to yield induced potential, screening charge densities, and interaction energies. Using the *ab initio* analysis described in Ref. 30, they were able to calculate various properties of the interactions between PMMA and the aluminum surface. However, the derivations are too involved for this review because the theoretical work involves both quantum and statistical mechanics; thus, the reader should consult the original reference.

For illustrating the various components of interaction energies, we choose to cite a simpler example of Pucciariello *et al.*[38] in the study of adhesion of methacrylic esters on a solid substrate. The conformation of the methacrylate monomer on the surface is shown in Figure 11. The interaction energy is given by the summation of the following components:

$$E \simeq E_\phi + E_\tau + E_b + E_{nb} + E_{el} + E_{hb} \qquad (12)$$

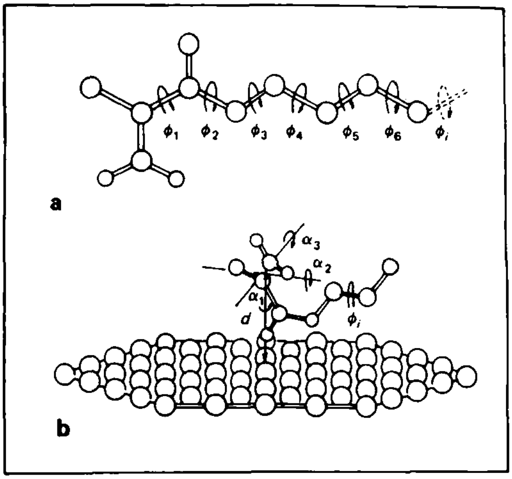


FIGURE 11 Conformation of a generic methacrylic monomer on a solid surface: a) Dihedral angles, ϕ_i, varied in the calculations for isolated monomers; b) geometrical parameters varied in the calculations for adsorbed monomers: d = distance between the center of the monomer, C=C bond and the surface, α_1, α_2, α_3 = Euler angles which define the orientation of the monomer towards the surface. Reprinted with permission from R. Pucciariello *et al.*, *Int. J. Adhes. Adhes.* 9(4), 205 (1989).

where E_ϕ is the torsion component; E_τ and E_b are the components associated with the deformation of bond angles and lengths, respectively; E_{nb} is the component between pairs of non-bonding atoms; E_{el} is the electrostatic component; and E_{hb} ($= E^{AB}$) is the hydrogen bonding component.

It is important to point out that the non-bonding (or van der Waals) interaction energy, E_{nb}, depends on the distance, r, between atoms. For very short distances between atoms, there is a repulsive energy; as r rises, the energy decreases until it reaches a minimum, at $r = r_0$. For values of r larger than r_0, the energy rises again, but remains less than zero, and that is the attractive force between the atoms. When r approaches infinity, the interaction energy approaches zero. The attractive energy is a function of r^{-6}, while the exact form of the repulsive term does not exist. The common expression is the same as that proposed by Lennard-Jones (LJ).[39] However, it should be noted that the LJ interactions alone are insufficient to describe strong interactions between a polymer and a metal surface.

Generally, in the conformational analysis, bond angles and lengths are kept constant, hence

$$E \simeq E_\phi + E_{nb} + E_{el} + E_{hb} \tag{13}$$

where E_ϕ is the energy associated with the rotation of a single bond. For a C—C bond not adjacent to a double bond, the rotation energy is given by

$$E_\phi = 1/2\, U_0(1 + \cos 3\phi) \tag{14}$$

where ϕ is the internal rotation angle and U_0 the intrinsic torsional barrier. In brief, the preliminary calculations carried out by Pucciariello *et al.*[38] allow the determination of the conformation of the monomers adsorbed on a charged surface, which is able to form hydrogen bonds with the monomers themselves. Furthermore, the calculations facilitate the evaluation of the changes of the conformational freedom, passing from isolated-top adsorbed monomers, and the examination of the flexibility of the ester side group for the monomers fixed in their minimum energy conformation on the surface.

The above discussion of the molecular modeling of polymers[40] and their interactions with solid surfaces is in an early stage, and there are still many challenges to be met before the modeling technique can become a viable tool for the polymer-metal adsorption and interaction studies.

Adhesion at Polymer-Metal Interface

Many of the above discussions are directly related to chemisorption. A direct first-principles calculation on polymer-metal adhesion has been carried out by Drabold and Adams.[41] Methane, ethylene, polyethylene and poly(methyl methacrylate) monomers are included for the *ab initio*, local orbital quantum molecular dynamics calculation. The aluminum [100] surface is a 32-atom slab cell (periodic in two dimensions and 4 layers deep). The preliminary study with CH_4 and C_2H_4 shows no attractive interaction as a function of molecular distance from the surface.

In the case of an apolar (or nonpolar) polymer, the stydy involves a rigid polyethylene oriented along the [110] direction of the Al [100] surface. A weak attractive interaction with a depth of about 0.045 eV is identified; however, a MD relaxation produces no additional binding. It appears that the completely passivated C atoms are entirely inactive in bonding with the Al surface.

A polar polymer, *e.g.*, PMMA, with a relaxed 17-atom rigid monomer segment as shown in Refs. 10 and 11, has been studied as a function of the height from the Al surface, with the carbonyl (C=O) group orienting near to the surface. There is only negligible binding between the PMMA and the Al surface. However, if the system is allowed to relax by weakening the carbonyl bond, the total binding energy differs by 2.4 eV from the separated to the chemisorbed system. Thus, the major effect of the chemisorption is to shift EDOS (electron density of states) to a slightly lower energy compared with the EDOS for Al and PMMA. It is important to note that the PMMA is not bonded to metal atoms, but to the metallic surface as a whole with the extended metallic eigenstates. In the following sections, we shall review some of the experimental results to illustrate the roles of chemisorption and molecular interactions in adhesion at polymer-metal interphases.

RESULTS OF MOLECULAR BONDING AND ADHESION AT POLYMER-METAL OXIDE INTERFACES

In a polymer-metal interfacial zone, there are different constituents, such as metal oxide, adsorbed contaminants, primer, etc. (Figure 12). Recently, some of the interactions have been discussed by Schultz.[42] In general, there are three types of interactions: 1) physical, 2) physicochemical, and 3) chemical. In this section, we focus on physicochemical and chemical interactions, except for the effects of contaminants, primers or

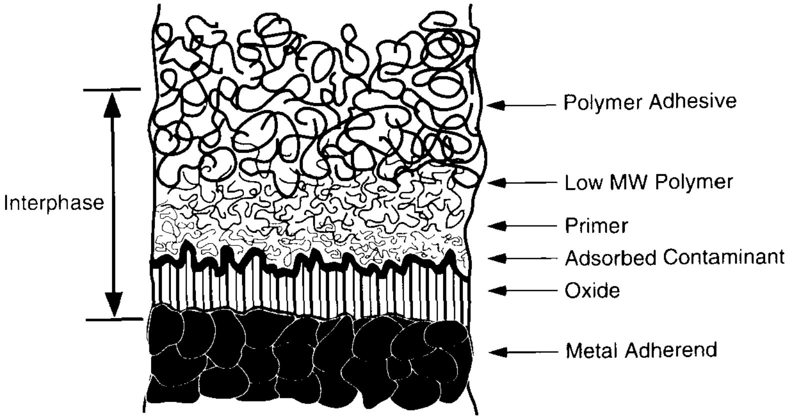


FIGURE 12 Polymer-Oxide-Metal Interphase.

coupling agents which should be treated in a separate paper. Our current discussion is limited to polymer-oxide and polymer-metal interfaces. As mentioned previously, the fractal dimensions of oxides are generally higher than those of the corresponding metals. Thus, there are more salient features for the oxide surfaces. For these two kinds of interfaces, we shall demonstrate that molecular bonding is evident, by theories and by experiments, in many instances.

Since the Lewis acid-base interaction is the major molecular interaction,[12-14] we should briefly discuss how to predict some of these interactions. By comparing acid- base strengths, metal oxides are generally more polar (or harder) than metals. For example, Cain and Matienzo[43] arranged the acid strengths of copper compounds as follows:

$$CuF_2 > CuO > CuF \simeq Cu_2O > Cu$$

In terms of chemical hardness, our calculated data show the same order. Thus, copper oxides are harder than copper.

Some oxides, *e.g.*, CaO, MgO, Al_2O_3, are Lewis bases, while others, *e.g.*, Fe_2O_3, Cr_2O_3, SiO_2, are Lewis acids. Following the HSAB principle,[15] hard acids prefer to react with hard bases. As a result, hard basic oxides react at a good rate with hard acids, *e.g.*, the carboxylic groups in a polymer. In the following examples, we can see why some of the interactions between polymers and oxides can take place rather readily from molecular interactions to chemical reactions at interphases.

Polyolefins on Metal Oxide Surfaces

For actual polymer-metal interphases, the polymer is more likely to interact with an oxide than a metal (Figure 12). However, the polymer-metal oxide interaction is still not well studied. In terms of polymers, Schultz *et al.*[44] have shown that grafting small quantities of acrylic acid onto polyethylene can enhance the adhesion to aluminum, and the acrylic groups appear to orient to the polymer/metal oxide interface. As a result, a chemical linkage is formed between the oxide and the oriented carboxylic groups. A concept of potential surface energy was introduced for a polymer. The surface energy is shown to depend on the environment and on the substrate in contact. Thus, this phenomenon also depends strongly on the orientation ability of the polymer.

Ulrén *et al.*[45] have also found that in hot-pressed laminates the polar groups, *e.g.*, carboxylic and butyl ester, actually engage in Lewis acid-base interactions with the aluminum oxide. The strength of the interfacial interactions depends on the acidity/basicity and the concentration of the functional group, the acid group being the most efficient.

Polyacrylic Esters on Metal Oxide Surfaces

Konstadinidis *et al.*[46] used XPS, infrared reflection-absorption spectroscopy (IRRAS), and solid state NMR to study the PMMA/aluminum interface. They have observed that PMMA adsorbs from the solution on the amorphous aluminum oxide surface, and the surface hydroxyl groups can hydrolyze the ester bond in the side chain of the polymer. As a result of the reaction, a side chain carboxylate ion is formed to bond ionically with the surface, and methanol is released as a byproduct. Thus, for polymer-metal oxide interactions, molecular bonding through chemisorption often leads to covalent bonding through a chemical reaction. The rotational conformations change at the segment level due to chemical interactions. These results suggest a flat configuration of the interfacial chains.

Polyimides on Metal Oxide Surfaces

Molecular bonding of PMDA-ODA polyimides (PI) and polyacrylic acid (PAA) ethyl ester with metal surfaces has been investigated with transmission electron microscopy (TEM) and a 90° peel test by Kim *et al.*[47] The adhesion strengths of polyimides on the metal surface are generally very high compared with that of metals atoms on polyimide. The Cr atom has the highest adhesion strength followed by Ni, Cu, and Au atoms. However, most metal surfaces are covered with a thin layer of metal oxides. Among them, Cr_2O_3 is rather corrosion resistant because of a protective layer forming over Cr. On the other hand, Cu oxide reacts readily with organic acids. Native Ni oxide lies somewhere in between. As a result, there are no Cr particles found in the polyimide. For the Ni substrate, only a few, if any, NiO particles are observed. However, some large particles are present as Cu_2O. The formation of particles has been postulated to be a process involving first the reaction of polyamic acid with Cu (or Ni) to form a polyamic acid complex. During the subsequent thermal curing, the complex decomposes to yield oxides which are then decomposed into aggregates to form particles during imidization. There is a precipitation-free zone due either to heterogeneous nucleation of the oxide particles or to temperature gradients during curing which causes the interfacial product to migrate from the vitrified polyimide into the still-plasticized polyamic acid.

Reactions of Epoxy Curing Agents with Metal Oxide Surfaces

Boerio and Ondrus[48] studied the polymer-metal oxide interphase with XPS and reflection-absorption infrared spectroscopy (RAIR or IRRAS). They have shown that in the case of the epoxide adhesive system, the anhydride curing agent, nadic methyl anhydride (NMA), reacts with the cuprous oxide on the copper substrate, and cuprous ions are removed from the oxide and oxidized, resulting in the formation of a layer of cupric carboxylate salt at the interphase. In the case of the 2024 aluminum substrate, the aluminum oxide also forms a surface carboxylate. The salt at the adhesive/adherend interface have been a weak boundary layer for the adhesive systems. This weak boundary layer will adversely affect the adhesive strength.

Reactions of Elastomers with Metal Oxide Surfaces

Elastomers like polybutadiene or its copolymers behave mysteriously on metal surfaces. In the case of polybutadiene, Watts and Castle[49] have identified with x-ray photoelectron spectroscopy (XPS) the presence of divalent iron at the polybutadiene mild steel oxide interphase. Polybutadiene is considered a Lewis base, and iron oxide is an acid. Thus, we should expect some molecular bonding at the interphase. However, polybutadiene is bonded to the mild steel through the formation of a discrete chemical interphase containing carboxylic groups. Presumably, polybutadiene later reduces the iron oxide, in contact, into ferrous species. The subsequent redox reaction may be common with transition metals. Thus, a similar redox reaction appears to take place at the polybutadiene-cobalt interphase.[3] In that case, the emission Mössbauer spectrum showed that Co^{3+} is reduced by polybutadiene to Co^{2+}. Moreover, the chemical nature of the interfacial region appears to change due to the continuous interactions, and emission Mössbauer spectra have detected the progress of the chemical aging. In most cases, the divalent ions increase with time and temperature.

Carré and Schultz[50, 51] have indicated that chemical interactions are more evident in the styrene-butadiene rubber (SBR) on the aluminum, presumably aluminum oxide, surface. Various surface treatments, *e.g.*, anodization, phosphatization, and sealing of the aluminum surface affect the adhesion at the elastomer-aluminum oxide interphase. They have found that these surface treatments can affect the degree of crosslinking of the elastomer. For example, in the case of phosphatized aluminum, the elastomer is 50 times more crosslinked than in the bulk; as a result, the cohesive strength near the interface is 40 times lower. In this case, chemical interaction appears to affect adversely the adhesive strength at the elastomer-metal interphase.

Contact Oxidation at the Polyolefin-Steel Interphase

In addition to the above redox reaction, contact oxidation has also been observed by Kalnins[52] at the polyolefin-steel interphase. The oxidation of polyethylene appears to be mainly noncatalytic on the surface, and homogeneously catalyzed in the bulk, but heterogeneously catalyzed at the polyethylene-metal interphase (Figure 13). Oxygen tends to diffuse through the polymer, and the catalyst adsorbs (or chemisorbs) at the cavities in the polymer-metal boundary. In the heterogeneous case, some metals may be oxidized into oxides at the interphases, and the presumed polymer-metal interactions are, in fact, polymer-oxide interactions. Thus, the interactions are actually contact oxidation, which can affect physical performance of the adhesive in various ways because oxidation can lead to crosslinking, transformation and some destructive processes. Consequently,

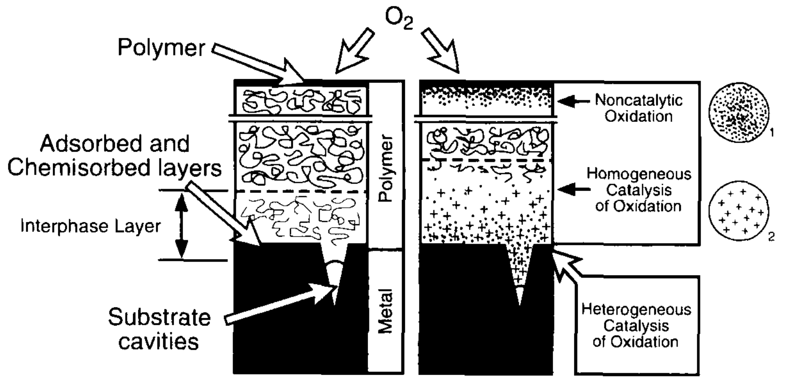


FIGURE 13 Contact oxidation at the polyolefin-steel interphase, reprinted with permission from M. M. Kalnins, *J. Adhesion.* 35, 173 (1991).

the polymer-metal system may indeed age as time progresses. The rates of the catalytic oxidation of polyolefins at elevated temperatures have been proposed to consist of two exponential functions.

RESULTS OF MOLECULAR BONDING AND ADHESION AT POLYMER-METAL INTERFACES

Metals are generally soft (less polar) in the chemical sense, and most of them are soft bases. Thus, most metals prefer to react with soft acidic groups in polymers. The grafting of acrylonitrile onto a metal is a good example of a soft acid-soft base interaction. We shall evaluate the following examples from the same point of view.

Previously, we discussed[12,13] Hoffmann's suggestion[53] that there is an additional interaction between a discrete molecule and the metal surface, which is near a continuum. The Fermi level is at the top of the valence band (or the occupied level), and electrons (or holes) will flow in the surface and in the bulk beneath it in an attempt to balance the interactions. However, this interaction influences only the second-order energetics and bonding resulting from the shift of electron density around the Fermi level.

Restructuring of Polar Groups of Grafted Polypropylene on the Aluminum Surface

As discussed in one of the earlier sections, a polymer adsorbed on a metal surface is in a nonequilibrium state.[40] Thus, polar (or hard) groups of polymer segments can restructure on metal surfaces. For example, a low molecular weight polypropylene grafted with maleic anhydride (MA) has been shown by Schultz *et al.*[54] with XPS, IR, and peeling experiments to migrate and reorient at the polymer-metal interphase. After the reorientation, chemical bonds are formed with hydroxyl groups on the metal surface. Secondly, the migration can lead to an enrichment of the interfacial zone in low molecular weight grafted polymeric chains; thus, a boundary layer of low cohesive strength is formed at the interphase. As a result, the peel energy increases with the MA content to a peak value and then decreases. Thus, molecular bonding tends to enhance adhesion but, in some cases, cannot overcome the adverse effect of the weak boundary layer.

Polyacrylic Ester Adhesive on the Aluminum Surface

SERS has become a powerful tool for the study of polymer-metal interphases.[55] With SERS, the Raman scattering cross section of molecules adsorbed onto the roughened surfaces of metals, such as Ag, Cu, and Au, is enhanced by as much as 10^6 relative to the normal cross section of free molecules. The enhancement can be explained by two mechanisms: 1) the long range mechanism (several adsorbed layers) is associated with electromagnetic resonances within a metallic substrate that enhance the electric field at the surface, and 2) the short range mechanism, especially for chemisorption, is related to the distortion of the molecular polarizability by the formation of charge-transfer complexes.

Boerio *et al.*[56] have examined a model of an acrylic adhesive system containing o-benzoic sulfimide (saccharin) and benzoic acid. The SERS spectrum of the adhesive is similar to that of saccharin,[57] which is a component of the adhesive curing system. Actually, saccharin adsorbs onto the Ag surface dissociatively. When saccharin of the curing system is replaced with benzoic acid, the SERS spectrum of the adhesive shows that of benzoic acid. The intensity of the SERS spectrum is independent of the thickness of the adhesive films, indicating that the observed Raman signal is characteristic of the interface and not the bulk of the films. Furthermore, saccharin and benzoic acid are preferentially adsorbed onto the Ag surface to form metal salts. This result demonstrates further that the SERS can be used for the nondestructive probing of polymer-metal interphases.

Polyimides on Metal Surfaces

Molecular bonding of polyimides to metal surfaces is manifested by two separate studies with SERS. Boerio *et al.*[58] have employed SERS to characterize the interface between an Ag island film and pyromellitic diimide (PMDI), a model compound for polyimide. PMDI is adsorbed (chemisorbed) end-on in a vertical conformation with one imide group adjacent to the surface. Since this type of acid-base interaction requires an intermolecular distance smaller than 4 Å, the PMDI away from the surface orients randomly without any adsorption to the metal surface. Thus, at the PMDI-Ag interphase, there are two kinds of PMDI: one chemisorbed to the metal surface and the other oriented randomly away from the surface.

Tsai *et al.*[59] have also studied the model of phthalimide (PIMH) adsorbed on the Ag island film. It was concluded that both PMDI and PIMH adsorb on the Ag surface end-on with one imide group adjacent to the surface. On the other hand, SERS spectra of *N*-phenylphthalimide and *N*,*N*′-diphenyl pyromellitic diimide adsorbed on the Ag surface show that the adsorption is edge-on with one *N*-phenylphthalimide (or two *N*,*N*′-diphenyl pyromellitic dimide) carbonyl group adjacent to the surface.

Grunze and Lamb[60] have examined vapor deposited ODA and PMDA on a polycrystalline silver substrate. Both compounds chemisorb on the clean surface under partial fragmentation. The adhesion of the polyimide film to the Ag surface involves chemical bonding to the two fragmented compounds originally chemisorbed on the substrate. This is another example showing that chemisorption through molecular bonding can lead to chemical reaction at the interphase.

Meyer *et al.*[61] have used the Langmuir-Blodgett (LB) technique to deposit ultrathin films of the dimethyldodecyl ammonium salt of PMDA-ODA polyamic acid (PACS) as 1-, 3- and 5- layer films on gold and silver surfaces. These films are imidized in the UHV system by heating to 523 K. A weak interaction is found for the first PI layer with the Au substrate. For thicker layers, a stoichiometric PI film is formed. However, on Ag, the interaction with the substrate is substantially stronger, leading to the inhibition of imidization in the first polymer layer. For thicker layers the imidization is also complete on the Ag surface as on the Au substrate. This work indirectly substantiates the molecular bonding results of Boerio *et al.*[58,59] for PMDI on the Ag surface using the SERS technique.

Epoxy Adhesives on Metal Surfaces

Curing agents in epoxy adhesives may react with the metal surface to form a bridge between the polymer and the metal surface. Tsai *et al.*[62] have studied the interaction between the Ag surface and an epoxy adhesive, the diglycidyl ether bisphenol A (DGEBA), which is cured with benzophenone tetracarboxylic dianhydride (BTDA). SERS results show that BTDA appears to adsorb preferentially on the Ag substrate. Young *et al.*[63] have applied SERS and XPS to investigate an epoxide adhesive containing a curing agent of 4, 4'-diaminodiphenylsulfone (DADPS or DDS) on the Ag surface. In this case, DADPS appears to adsorb through one of the amino groups with an end-on conformation. A large amount of Ag is on the substrate fracture surface, while only a trace of it remains on the adhesive fracture surface. Thus, the failure of the adhesive is within the interphase but nearer to the Ag substrate.

Péchereaux *et al.*[64] have reported that for an interphase of chemical origin, the type of metal can influence the crosslink density of the epoxy resin close to the metal surface. The mechanism of this effect on the crosslink density is still not clear. Though the failure is cohesive, the shear strength increases about 80% when going from gold to aluminum. Moreover, nickel appears to induce some reaction at the interphase.

Redox Reactions between Dicyandiamide in Epoxy and Metal Surfaces

In some epoxy adhesives, dicyandiamide (dicy) is incorporated to function only as a curing agent. However, the following results may indicate that it is also functioning as a coupling agent between epoxy resin and metal surfaces. Boerio and Hong[65] have used the SERS spectra to study the interaction of dicy with the Ag surface. The spectrum indicates that dicy adsorbs (chemisorbs) with a vertical configuration involving coordination through the nitrilo nitrogen atom. The same configuration is also evident for an 8:1 mixture of DGEBA and dicy. These results indicate that dicy is preferentially adsorbed between the adhesive and the Ag surface, and that the interphase is likely to be enriched with dicy in comparison with the bulk adhesive.

Carter *et al.*[66] have applied infrared reflection-adsorption spectroscopy to study the reaction of the neat dicyandiamide on the zinc surface and the dicy crosslinked epoxy adhesive on the zinc and steel surfaces. No spectral changes are observed when dicy is heated on steel or ZnO-coated steel. However, dicy is reduced through the reaction specifically with the Zn surface.

Holubka and Ball[67] have employed a semi-empirical MNDO molecular model to verify the above IR results for epoxy adhesives/galvanized steel adhesion. The calculations indicate that one tautomeric form of dicy, the diamino form, is the most stable structure by about 9.3 kcal/mol. The molecule appears to be a π-system, largely isoelectronic with butadiene. The symmetry and the magnitude of atomic orbitals of the LUMO of the diamino form of dicy are consistent with the suggested form of a radical anion reduction product, which yields a carbodiimide intermediate on the Zn surface (Figure 14).

SUMMARY

In this review, we first briefly discussed the fractal nature of polymer-metal interphases. Then we discussed the fundamentals of molecular bonding between polymer and metal at the interphases. In general, interphases are more complex than interfaces. It appears that polymer-metal interphases are gradient, indefinite, and dynamic. For the simplest cases, our discussion did not involve contaminants, primers or coupling agents.

We cited several theoretical studies related to molecular modeling and quantum-chemical calculations for the metal surfaces, first with organic molecules or monomers, and then with models of polymers. These approaches are rather enlightening, but at an early stage, and there are still some challenges that must be met before the theoretical methods can be widely adopted for the study of polymer-metal interphases.

In contrast, experimental studies with XPS, SERS and Mössbauer emission spectroscopy are more informative in demonstrating various molecular bonding at polymer-metal interphases. Generally, molecular bonding leads to chemisorption and/or chemical reactions. It appears that metal oxides are more reactive than metals. These chemical interactions, especially contact oxidation, may eventually affect adhesion and adhesive joints in various ways. Some strong chemical interactions at the polymer-

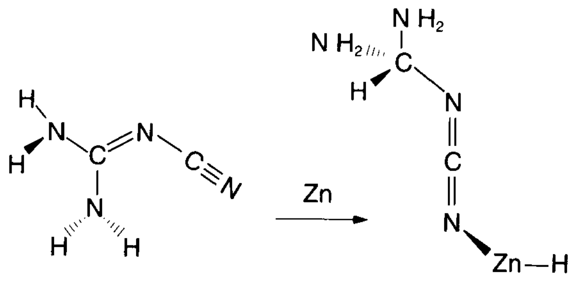


FIGURE 14 Reaction of dicyandiamide on the zinc surface, reprinted with permission from J. W. Holubka and J. C. Ball, *J. Adhes. Sci. Technol.* 4, 443 (1990).

metal interphase can create a weak boundary layer and may not always be beneficial to adhesion and physical properties.

NOMENCLATURE

D_a	fractal dimension of the surface
D_c	chemisorptive fractal dimension
E_ϕ	torsion component of the interaction energy
E_τ	bond angle deformation component
E_b	bond length deformation component
E_{el}	electrostatic component
E_{hb}	hydrogen bonding component
E_{nb}	nonbonding component
$E_{xc}[n(\mathbf{r})]$	exchange energy
m	amount of polymer physically adsorbed
M	number of nuclei in the molecule
m_c	amount of polymer chemisorbed
M_w	molecular weight of a polymer
$n(\mathbf{r})$	electron density distribution
$\mathbf{r}(or\ \mathbf{r}')$	spatial coordinates
r_a	effective horizontal radius
r_s	Wigner-Seitz radius
$T_s[n(\mathbf{r})]$	kinetic energy of noninteracting electronic system
U_o	intrinsic torsion barrier
V_{ap}	Flory-type exponent
$V^{ex}(\mathbf{r})$	external potential with the electron density
Z	atomic number
z	coordinate normal to the surface

Greek Letters

β	geometry-related coefficient
ξ_i	van der Waals radius of atom i
μ	Lagrange multiplier or chemical potential
ρ	average density of valence electron
ρ^{EX}	positive charge background density
ϕ	internal rotation angle
χ_i	total electron count for each atom

References

1. L. H. Sharpe, *J. Adhesion* **4**, 5 (1972), also in: *Recent Advances in Adhesion*, L. H. Lee, Ed. (Gordon and Breach, New York, 1972), p. 437.
2. J. D. Miller and H. Ishida, in *Fundamentals of Adhesion*, L. H. Lee, Ed. (Plenum Press, New York, 1991), Chapt. 10.

3. H. Leidheiser, Jr. and P. D. Deck, *Science* **241**, 1176 (1988).
4. R. P. Wool, in *Fundamentals of Adhesion*, L. H. Lee, Ed. (Plenum Press, New York, 1991), Chapt. 7.
5. D. Avnir and D. Farin, *New J. Chem.* **14**, 197 (1990).
6. D. Farin and Avnir, *Colloids Surf.* **37**, 155 (1989).
7. D. Avnir, D. Farin, and P. Pfeifer, *New J. Chem.* **16**, 439 (1992).
8. P. S. Ho, R. Haight, R. C. White, B. D. Silverman and F. Faupel, in *Fundamentals of Adhesion*, L. H. Lee, Ed. (Plenum Press, New York, 1991), Chapt. 14.
9. N. J. di Nardo, *Proceedings of Symposium on Metallized Plastics. Fundamental and Applied Aspect*, Electrochemical Society Meeting, October, 1988.
10. A. K. Chakraborty, H. T. Davis, and M. Tirrell, *J. Polym. Sci. A. Polym. Chem.* **28**, 3185 (1990).
11. A. K. Chakraborty, in *Polymer-Solid Interfaces*, J. J. Pireaux, P. Bertrand, and J. L. Bredas, Eds. (Institute of Physics, Bristol, U. K., 1992), p. 3.
12. L. H. Lee, *J. Adhes. Sci. Technol.* **5**(1), 71 (1991).
13. L. H. Lee, *J. Adhesion* **37**, 187 (1992).
14. L. H. Lee, *J. Adhesion* **36**, 39 (1991).
15. R. G. Pearson, *J. Am. Chem. Soc.* **85**, 3533 (1963).
16. J. Ferrante and J. R. Smith, *Phys. Rev.* **B 19**(8), 3911 (1979).
17. A. Banerjea, J. Ferrante, and J. R. Smith, in *Fundamentals of Adhesion*, L. H. Lee, Ed. (Plenum Press, New York, 1991), Chapt. 11.
18. L. H. Lee, *J. Adhes, Sci. Technol.* 7(6), 583 (1993).
19. J. J. Pireaux *et al.*, in *Adhesion and Friction*, M. Gunze and H. Kreuzer, Eds. (Springer, Verlag, Berlin 1989).
20. J. A. Rodriguez, *Surf. Sci.* **273**, 385 (1992).
21. J. A. Rodriguez, *Langmuir* **7**, 1206 (1991).
22. S. Fujii, Y. Misono and K. Itoh, *Surf. Sci.* **277**, 220 (1992).
23. C. Boiziau and G. Lécayon, *Int. J. Adhes. Adhes.* **6**(4), 207 (1986).
24. C. Boiziau and G. Lécayon, *Surf. Interface Anal.* **12**, 475 (1988).
25. C. Boiziau, *Pure & Appl. Chem.* **64**(11), 1647 (1992).
26. G. Deniau, P. Viel, G. Lécayon, and J. Delhalle, *J. Surf. Interface Anal.* **18**, 443 (1992).
27. E. Léonard-Stibbe *et al.*, in *Polymer-Solid Interfaces*, J.J. Pireaux, P. Bertrand, and J.L. Bredas, Eds. (Institute of Physics, Bristol, UK, 1992), p. 93.
28. J. Holubka, R. A. Dickie, and J. C. Cassatta, *J. Adhes. Sci. Technol.* **6**(2), 243 (1992).
29. J. S. Shaffer and A. K. Chakraborty, *Polymer Preprints* **31**(2), 546 (1990).
30. J. S. Shaffer, A. K. Chakraborty, M. Tirrell, H. T. Davis, and J. L. Martins, *J. Chem. Phys.* **95**(11), 8616 (1991).
31. A. K. Chakraborty, J. S. Shaffer, and P. M. Adriani, *Macromolecules* **24**, 5226 (1991).
32. P. Hohenberg and W. Kohn, *Phys. Rev. B.* **136**, 864 (1964).
33. A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1989).
34. N. D. Lang in *Theory of the Inhomogeneous Electron Gas*, S. Lundqvist and N. H. March, Eds. (Plenum Press, New York, 1983), pp. 309–389.
35. N. D. Lang and W. Kohn, *Phys. Rev. B.* **136**, 864 (1964).
36. W. A. de Heer, P. Milani, and A. Chàtelain, *Phys. Rev. Lett.* **63**(26), 2834 (1989).
37. A. K. Chakraborty and P. M. Adriani, *Macromolecules* **25**, 2470 (1991).
38. R. Pucciariello, N. Bianchi, and R. Fusco, *Int. J. Adhes. Adhes.* **9**(4), 205 (1989).
39. J. E. Lennard-Jones and B. M. Dent, *Trans. Faraday Soc.* **24**, 92 (1928).
40. D. N. Theodorou, in *Physics of Polymer Surfaces and Interfaces*, I.C. Sanchez, Ed. (Butterworth-Heinemann, Boston, and Manning, Greenwich, 1992), Chapt. 7.
41. D. A. Drabold and J. B. Adams, submitted to *Phys. Rev. Lett.*, 1992.
42. J. Schultz, *J. Adhesion* **37**, 73 (1992).
43. S. R. Cain and L. J. Matienzo, *J. Adhes. Sci. Technol.* **2**(5), 395 (1988).
44. J. Schultz, A. Carré, and C. Mazeau, *Int. J. Adhes. Adhes.* **4**(4), 163 (1984).
45. L. Ulrén, T. Hjertberg, and H. Ishida, *J. Adhesion* **31**, 117 (1990).
46. K. Konstadinidis, B. Thakkar, A. Chakraborty, L. W. Potts, R. Tannenbaum, and M. Tirrell, *Langmuir* **8**, 1307 (1992).
47. Y. H. Kim, J. Kim, G. F. Walker, C. Feger, and S. P. Kowalezyk, *J. Adhes. Sci. Technol.* **2**(2), 95 (1988).
48. F. J. Boerio and D. J. Ondrus, *J. Colloid Interface Sci.* **139**, 446 (1990).
49. J. F. Watts and J. E. Castle, *J. Mater. Sci.* **18**, 2987 (1990).
50. A. Carré and J. Schultz, *J. Adhesion* **17**, 135 (1984).
51. J. Schultz and A Carré, *J. Appl. Polym. Sci., Appl. Polym. Symp.* **39**, 103(1984).
52. M. M. Kalnins, *J. Adhesion* **35**, 173 (1991).

53. R. Hoffmann, *Solids and Surface-A Chemist's View of Bonding in Extended Structure* (VCH Publishers, Weinheim, 1988).
54. J. Schultz, L. Lavielle, A. Carré, and P. Comien, *J. Mat. Sci.* **24**, 4363 (1989).
55. R. K. Chang and T. E. Furtak, Eds., *Surface Enhanced Raman Scattering* (Plenum Press, New York, 1982).
56. F. J. Boerio, P. P. Hong, P. J. Clark, and Y. Okamoto, *Langmuir* **6**, 721 (1990).
57. F. J. Boerio, P. P. Hong, W. H. Tsai, and J. T. Young, *Surf. Interface Anal.* **17**, 448 (1991).
58. F. J. Boerio, L. J. Young, W. H. Tsai, and S. J. Clarson, *Polym. Prepr.* **31**(2), 554 (1990).
59. W. H. Tsai, J. T. Young, F. J. Boerio, and P. P. Hong, *Langmuir* **7**, 745 (1991).
60. M. Grunze and R. N. Lamb, *Chem. Phys. Lett.* **133**(4), 283 (1987).
61. W. Meyer, M. Grunze, R. Lamb, A. Ortega-Vilamil, W. Schrepp and W. Braun, *Surf. Sci.* **273**, 205 (1992).
62. W. H. Tsai, J. T. Young, and F. J. Boerio, *J. Adhesion* **33**, 211 (1991).
63. L. J. Young, N. G. Cave, and F. J. Boerio, *J. Adhesion* **37**, 143 (1992).
64. V. Péchereaux, J. Schultz, Z. Duteurtre, and J. P. M. Gombert, *Proc. 2nd. Intl. Conf. on Adhesion and Adhesives*, ADHECOM '89, **1**, 103 (1989).
65. F. J. Boerio and P. P. Hong, *Mat. Sci. Eng.* **A 126**, 245 (1990).
66. R. O. Carter, III., R. A., Dickie, J. W. Holubka, and N. E. Lindsay, *Ind. Eng. Chem. Res.* **28**, 48 (1989).
67. J. W. Holubka and J. C. Ball, *J. Adhes. Sci. Technol.* **4**(6), 443 (1990).