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Investigation of the Impact of Cleaning on the Adhesive Bond and the Process Implications

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Investigation of the Impact of Cleaning on the Adhesive Bond and the Process Implications

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Abstract

While surface cleaning is the most common process step in DOE manufacturing operations, the link between a successful adhesive bond and the surface clean performed before adhesion is not well understood. An innovative approach that combines computer modeling expertise, fracture mechanics understanding, and cleaning experience to address how to achieve a "good" adhesive bond is discussed here to develop a capability that would result in reduced cleaning development time and testing, improved bonds, improved manufacturability, and even an understanding that leads to improved aging. A simulation modeling technique, polymer reference interaction site model applied near wall (Wall PRISM), provided the capability to include contaminants on the surface. Calculations determined an approximately 8% reduction in the work of adhesion for 1% by weight of ethanol contamination on the structure of a silicone adhesive near a surface. The demonstration of repeatable coatings and quantitative analysis of the surface for deposition of controlled amounts of contamination (hexadecane and mineral oil) was based on three deposition methods. The effect of the cleaning process used on interfacial toughness was determined. The measured interfacial toughness of samples with a Brulin cleaned sandbasted aluminum surface was found to be ~15% greater than that with a TCE cleaned aluminum surface. The sensitivity of measured fracture toughness to various test conditions determined that both interfacial toughness and interface corner toughness depended strongly on surface roughness. The work of adhesion value for silicone/silicone interface was determined by a contact mechanics technique known as the JKR method. Correlation with fracture data has allowed a better understanding between interfacial fracture parameters and surface energy.

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PREFACE

Surface cleaning is the most common process step in DOE manufacturing operations. For example, approximately 75% of Honeywell/FM&T's critical process steps for weapons manufacture involve surface cleaning or preparation. We do not understand the link between a successful adhesive bond and the surface clean performed before adhesion. When qualifying a new solvent for weapons manufacture, the cleaning engineer must rely on cumbersome laboratory tests, which are expensive, repetitious, and time consuming. For many years, the cleaning community has called for an understanding of "how clean is clean?" Very little work has been done in this area since it requires a fundamental understanding of the process following the clean. This proposal, applying our computer modeling expertise, fracture mechanics understanding, and cleaning experience, is innovative in that we are addressing the issue of how do we achieve a "good" adhesive bond. Modeling has not been commonly used to deal with cleaning processes in the past. Understanding the link between surface preparation and adhesion would result in reduced cleaning development time and testing, improved bonds, improved manufacturability, and may result in an understanding that leads to improved aging. This capability can ultimately be applied to agile manufacturing tools. Developing a validated model for cleaning and surface preparation in adhesive bonding, coating, encapsulation, or painting processes would complete Sandia's capability for a process that assures efficient and low cost production of small lots.

NOMENCLATURE

ADCB	Asymmetric Double Cantilever Beam
AES	Auger Electron Spectroscopy
AFM	atomic force microscopy
CA	contact angle
DFT	Density Functional Theory
DIW	deionized water
JKR	The JKR theory is a continuum mechanics model of the contact for two solid spheres that was developed by Johnson, Kendall and Roberts
MD	Molecular Dynamics
MESERAN	Measurement and Evaluation of Surfaces by Evaporative Rate Analysis
PDMS	polydimethyl siloxane
PFA	perfluoroalkoxy
PIB	polyisobutylene
PY	Percus-Yevick
TCE	trichloroethylene
TOF SIMS	time-of-flight secondary ion mass spectroscopy
Wall PRISM	Polymer Reference Interaction Site Model Applied Near Wall

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Investigation of the Impact of Cleaning on the Adhesive Bond and the Process Implications

INTRODUCTION

The Manufacturing Science and Technology LDRD investment area develops advanced manufacturing and production technologies with an emphasis on moving the product from the design stage to accepted hardware. Efforts to reduce cost, shorten the design and manufacturing cycle, and improve predictability of products are encouraged. Programmatic areas include two main thrusts: (1) Develop processes that enable defect and cost reduction, or enable the manufacture of emerging product technologies. (2) Provide new processes that reduce product fabrication or service defects. These will reduce product development time and expense.

About 75% of critical process steps for weapons manufacture involve surface cleaning or preparation, making surface cleaning the most common process step in DOE manufacturing operations. When an engineer qualifies a new solvent for weapons manufacture, he must rely on cumbersome laboratory tests, which are expensive, repetitious, and time-consuming. After machining metals, an engineer must remove the lubricants used in the machining process, but many cleaners that we once used are now banned because of ozone depletion regulations. Frequently the engineer will clean and bond the part, only to have the joint fail in test – often leading to the assumption that the cleaning was inadequate. Overcleaning is a concern because it increases the waste stream. On the other hand, it increases the product cycle time, and leads to increased product cost.

By applying our computer-modeling expertise, fracture mechanics understanding, and cleaning experience, we explored out how clean a surface must be to achieve a good adhesive bond. Understanding the link between surface preparation (both cleanliness and roughness) and adhesion can lead to reduced cleaning development time and testing, improved bonds, and improved manufacturability, which can be applied to agile manufacturing tools and will help advance product realization for encapsulated components. Developing a validated model for cleaning and surface preparation in adhesive bonding, coating, encapsulation, or painting processes would complete Sandia's capability for a process that ensures efficient, low-cost production of small lots.

MOLECULAR MODELING

INTRODUCTION

Consider a low molecular weight contaminant near an interface between a polymer adhesive and a substrate. Depending on the substrate-polymer and polymer-polymer interactions, as well as the molecular architecture of the contaminant and polymer, the contaminant may preferentially adsorb to the interface. When this happens, the contaminant molecules will displace the polymer from the interface resulting in a degradation of the adhesive bond strength. This effect is shown schematically in Figure 1. The purpose of this effort is to quantify this effect using molecular modeling.

Figure 1- Effect of Contamination on an Adhesive Bond.

There are three statistical mechanical methods that can be used to compute the interfacial polymer structure: Wall PRISM theory¹, Density Functional Theory^{2,3} (DFT), and full molecular dynamics or Monte Carlo simulation. This report focuses on with the theoretical techniques of Wall PRISM and DFT. Because full computer simulation requires large computational resources it does not lend itself readily to being used as an engineering tool and is not be considered here.

WALL PRISM THEORY

The polymer RISM or PRISM theory of Curro and Schweizer for bulk amorphous polymers and mixtures has been discussed in detail in previous publications⁴⁻⁶ and will only be briefly sketched here. A polymer chain consists of N monomers and each is constructed from N_s overlapping

spherical sites. Examples of the united atom representation of a vinylidene polymer are shown in Figure 2.

Figure 2- United Atom Representation of a Vinylidene Polymer. For PDMS sites type A correspond to Si atoms, type B correspond to O atoms, and type C correspond to pendant methyl groups.

From the generalized Ornstein-Zernike equation of Chandler and Andersen⁷, we can relate the intermolecular radial distribution functions of the bulk polymer $g_{\alpha\gamma}(r)$ to the average intramolecular structure $\hat{\Omega}_{\alpha\gamma}(k)$ of a single polymer chain,

$$\hat{H}(k) = \hat{\Omega}(k) \cdot \hat{C}(k) \cdot [\hat{\Omega}(k) + \hat{H}(k)] \quad (1)$$

where the caret denotes the 3-dimensional Fourier transform with wavevector k .

$$\begin{aligned} \hat{f}(k) &= \int f(r) e^{-i\vec{k} \cdot \vec{r}} d\vec{r} \\ f(r) &= \frac{1}{8\pi^3} \int \hat{f}(k) e^{i\vec{k} \cdot \vec{r}} d\vec{k} \end{aligned} \quad (2)$$

The intermolecular correlation matrix is defined from the individual radial distribution functions between sites of type α and γ on different polymer chains,

$$\begin{aligned} H_{\alpha\gamma}(r) &= \rho_{\alpha} \rho_{\gamma} h_{\alpha\gamma}(r) \\ &= \rho_{\alpha} \rho_{\gamma} [g_{\alpha\gamma}(r) - 1] \end{aligned} \quad (3)$$

where ρ_α is the density of sites of type α . The intramolecular structure factor can be defined, for convenience, in Fourier transform space according to

$$\hat{\Omega}_{\alpha\gamma}(\mathbf{k}) = \frac{\rho_\alpha}{N} \sum_{i \in \alpha} \sum_{j \in \gamma} \left\langle \frac{\sin \mathbf{k} \mathbf{r}_{ij}}{k r_{ij}} \right\rangle \quad (4)$$

between sites of type α and γ on the same chain.

The matrix elements $C_{\alpha\gamma}(\mathbf{r})$ in Eq. (1) are the direct correlation functions that are approximated through the Percus-Yevick (PY) approximation⁸ (or closure)

$$\begin{aligned} g_{\alpha\gamma}(\mathbf{r}) &= 0 \quad \text{for } r < d_{\alpha\gamma} \\ C_{\alpha\gamma}(\mathbf{r}) &\equiv 0 \quad \text{for } r > d_{\alpha\gamma} \end{aligned} \quad (5)$$

where we have employed the hard sphere potential with hard core diameter d .

Thus, the generalized Ornstein-Zernike relation, Eq. (1), together with the approximate closure, Eq. (5), provide a relationship between the intermolecular structure characterizing the packing of a polymer melt and the intramolecular structure of the polymer. All the information regarding the polymer architecture enters the theory through the functions $\hat{\Omega}_{\alpha\gamma}(\mathbf{k})$. In practice, these functions are obtained from a separate single chain calculation or computer simulation using the Flory ideality hypothesis⁶. Good agreement has been found between PRISM theory and full multichain computer simulations^{9,10} and with wide-angle x-ray scattering experiments on polyethylene¹¹ and polypropylene melts¹².

In order to construct Wall PRISM theory¹, we now consider the equilibrium between spherical solute sites and a polymer melt in the zero concentration limit of the solute. The polymer is composed of identical monomers each containing N_s different sites of type $\alpha = A, B, C$, etc. For this situation, the polymer/solute cross correlation function $g_\alpha(\mathbf{r}) = h_\alpha(\mathbf{r}) + 1$ between a site of type α on a polymer chain and the solute can be obtained from the generalized Ornstein-Zernike equation after algebraic manipulation:

$$\rho_\alpha \hat{h}_\alpha(\mathbf{k}) = \sum_\gamma \hat{S}_{\alpha\gamma}(\mathbf{k}) \hat{C}_\gamma(\mathbf{k}) \quad (6)$$

where $\hat{S}_{\alpha\gamma}(\mathbf{k}) = \hat{\Omega}_{\alpha\gamma}(\mathbf{k}) + \hat{H}_{\alpha\gamma}(\mathbf{k})$ is the partial structure factor of the pure polymer melt.

We consider a special case¹ where the solute particle consists of a spherical core of radius R_1 , surrounded by a spherical shell of inner radius R_2 and outer radius R_3 (see Figure 3). We now take the limit as R_1 , R_2 , and R_3 approach infinity such that $R_2 - R_1 = H$. For the case when the polymer resides in the range $R_1 < r < R_2$, the limit corresponds to a polymer melt in a slit of width H .

Figure 3- A Schematic of the Solute Particle Used to Construct Wall PRISM Theory. The polymer is visualized to occupy the shaded annulus. The limit is taken as R_1 , R_2 , and R_3 approach infinity such that $R_2 - R_1 = H$ remains finite.

To facilitate taking the above limit, it is convenient to express Eq. (6) in real space using the 3-dimensional convolution theorem and bipolar coordinates:

$$\rho_\alpha h_\alpha(r) = \frac{2\pi}{r} \sum_\gamma \int_0^\infty t S_{\alpha\gamma}(t) dt \int_{|r-t|}^{r+t} y C_\gamma(y) dy \quad (7)$$

where r is the position of site α on the polymer with respect to the origin defined in Figure 3; t and y are dummy variables. We now change variables to z and s so that the origin is exactly between the inner and outer surfaces of the annulus.

$$z = r - \left(R_1 + \frac{H}{2} \right) \quad (8)$$

$$s = y - \left(R_1 + \frac{H}{2} \right)$$

In the limit as $R_1 \rightarrow \infty$ Eq. (7) becomes

$$\rho_\alpha h_\alpha(z) = 2\pi \sum_\gamma \int_0^\infty t S_{\alpha\gamma}(t) dt \int_{|z-t|}^{z+t} C_\gamma(s) ds \quad (9)$$

From the PY closure of Eq. (5) we now have the condition

$$g_{\alpha}(z) = 0, \quad |z| > \frac{H}{2} \quad (10)$$

$$C_{\alpha}(z) \equiv 0, \quad -\frac{H}{2} < z < \frac{H}{2}$$

Note that $\lim_{z \rightarrow \infty} C_{\alpha}(z)$ is nonzero. This condition is inconvenient for the use of Fourier transforms, hence we define a modified direct correlation function $C_{\alpha}^*(z)$, which is constructed to approach zero for large z :

$$C_{\alpha}^*(z) = C_{\alpha}(z) + a_{\alpha} \quad (11)$$

$$a_{\alpha} = -\lim_{z \rightarrow \infty} C_{\alpha}(z)$$

Using the condition that $\lim_{z \rightarrow \infty} g_{\alpha}(z) = 0$ it is possible to express a_{α} in terms of the zero wavevector structure factor of the polymer melt:

$$a_{\alpha} \equiv a = \rho_{\alpha} \hat{S}_{\alpha\alpha}^{-1}(0) = \frac{\rho_A}{N_s \hat{S}_{AA}(0)} \quad (12)$$

Eq. (9) can now be recast in terms of the new variable $C_{\alpha}^*(z)$:

$$\rho_{\alpha} g_{\alpha}(z) = 2\pi \sum_{\gamma} \int_0^{\infty} t S_{\alpha\gamma}(t) dt \int_{|z-t|}^{z+t} C_{\alpha}^*(s) ds \quad (13)$$

The above equation can be written in a compact form by employing the 1-dimensional convolution theorem:

$$\rho_{\alpha} \tilde{g}_{\alpha}(k) = \sum_{\gamma} \hat{S}_{\alpha\gamma}(k) \tilde{C}_{\gamma}^*(k) \quad (14)$$

where the tilde represents the 1-dimensional Fourier transform defined as

$$\tilde{f}(k) = \int_{-\infty}^{\infty} f(z) e^{-izk} dz \quad (15)$$

$$f(z) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{f}(k) e^{izk} dk$$

Note that Eq. (14) combines both the 3-dimensional Fourier transform of the structure factor matrix as well as the 1-dimensional transforms of the correlation functions. It is interesting to note that the only information regarding the nature of the polymer enters the theory through the structure factor matrix $\hat{S}_{\alpha\gamma}(k)$. This is obtained by first using PRISM theory to solve for the structure of the polymer melt. Once having the structure factors of the bulk polymer, Wall PRISM theory then employs Eq. (14), together with the closure condition

$$g_{\alpha}(z) = 0, \quad |z| > \frac{H}{2} \quad (16)$$

$$C_{\alpha}^{*}(z) \cong \frac{\rho_A}{N_s \hat{S}_{AA}(0)}, \quad -\frac{H}{2} < z < \frac{H}{2}$$

to obtain the distribution of each of the sites $\alpha = A, B, C$, etc. between the walls.

Two features of Wall PRISM require special mention. The first feature is that in the above formulation of the theory, the influence of the wall on the chain conformations and fluid-fluid correlations near the surface is completely ignored. In principle, one might be able to incorporate such effects either through an improved closure, or through a self-consistent calculation that allows for chain expansion near the wall. The second feature is that the accuracy of the PRISM/PY approach when large disparities in atomic size are present is unknown; the Wall PRISM theory focuses on the limit when the size ratio is infinite. For binary hard sphere mixtures the PY theory is known to become less accurate as the size ratio is increased. These possible deficiencies notwithstanding, Wall PRISM theory is a very convenient route to the structure of hard chains when compared to the alternatives.

The Wall PRISM theory is embodied in Eqs. (14) and (16). These equations can be solved numerically in a straightforward manner using Picard iteration techniques^{4,6}. For the special case of a melt of threadlike polymers¹², it is even possible to obtain a simple analytical solution to the Wall PRISM equations. In this section, we will present solutions of the Wall PRISM theory for a series of specific polymer models with progressively more chemical realism in the monomeric structure.

We consider the case of alkane chains modeled with the rotational isomeric state model¹³. Vacatello, Yoon, and Laskowski¹⁴ performed MD simulations on tridecane ($C_{13}H_{28}$) alkane

molecule liquids interacting with Lennard-Jones potentials near a neutral wall. Their results are shown as the points in Figure 4. Since the PRISM calculation was performed with hard core potentials between overlapping methylene groups, rather than the soft repulsions used in the simulation, the equivalent hard core diameter used was determined to be $d=3.32$ Å from Barker-Henderson theory⁸. The curve in Figure 4 was obtained from numerical solution of Eqs. (14) and (16) using PRISM theory for the bulk liquid alkane¹¹ using the structure factor in Eq. (14). An important difference between the simulation and the Wall PRISM calculation was that the simulations included attractive intermolecular interactions between methylene groups, while the corresponding interactions were purely hard-core in the Wall PRISM calculation. Unfortunately, the Lennard-Jones interactions employed by Vacatello and coworkers¹⁴ were significantly weaker than would be expected for a real alkane liquid.

Figure 4 - Alkane Liquids Near a Hard Wall. The main figure depicts results for tridecane, $C_{13}H_{28}$, from the MD simulations (points) of Vacatello, Yoon, and Laskowski¹⁴, and Wall PRISM theory (solid curve) with a hard core diameter of $d=3.32$ Å and $\rho_0=0.03192/\text{Å}^3$. The inset is the Wall PRISM prediction for polyethylene of $N=6429$ and $T=430$ K.

It can be observed from Figure 4 that the simulation exhibits a maximum in the distribution of CH_2 units at about 1 Å from the wall. By contrast, the Wall PRISM profile does not show this peak but instead monotonically approaches the wall with a higher contact value. On longer length scales, beyond about 2 Å, it can also be seen that Wall PRISM agrees fairly well with the simulation. As will be discussed later, the probable origin of the disagreement very close to the wall is the inability of the theory to account for the effect of the attractive intermolecular interactions.

Wall PRISM theory was used to calculate the distribution of methylene groups in a polyethylene melt ($N=6429$, $T=430$ K) near a hard wall. These results are shown in the inset in Figure 4. As in the case of the 13-unit alkane, the rotational isomeric state model was used along with PRISM

theory for the homogeneous, polymer liquid. For polyethylene, we employed a hard-core diameter of $d=3.9 \text{ \AA}$ that was determined previously¹¹ from comparisons with wide-angle x-ray scattering experiments. Note that the distribution of methylene groups in polyethylene is qualitatively similar to $C_{13}H_{28}$. Again, no maximum is found from Wall PRISM theory in the immediate vicinity of the wall. The surface structure of the polyethylene melt persists farther into the liquid ($\sim 15 \text{ \AA}$) than for the shorter chain alkane liquid ($\sim 10 \text{ \AA}$). This is due to the larger radius of gyration of polyethylene that extends the range of the correlation hole.

We can also employ Wall PRISM theory to model more complex chain architectures such as the polydimethyl siloxane (PDMS) structure shown schematically in Figure 2.

Figure 5 - Wall PRISM Predictions for PDMS Near a Hard Wall. The figure shows the relative site distributions, where $g_w(z)$ is the site density (normalized by the bulk density) of type $\alpha=A,B,C$ in the bulk liquid. The bulk density was $0.00796/\text{\AA}^3$.

Weinhold and Curro¹⁵ have modeled both polyisobutylene (PIB) and polydimethyl siloxane (PDMS) melts with PRISM theory. For PDMS we take the A site to be an oxygen atom, the B site a silicon atom, and the two C sites as methyl groups. The modeling consisted of solving the PRISM theory self-consistently to obtain the 6 partial structure factors for PDMS in the bulk state. This was then used as input to the Wall PRISM theory; the results for packing of PDMS against a neutral substrate are shown in Figure 6. Note that, as expected, the pendant methyl groups preferentially pack near the substrate since these groups are on the outside of the chains. At the same time, the backbone Si and O atoms are shielded by the side groups from making contact with the surface.

We now consider the case of a polymer mixed with a low molecular contaminant near a substrate. For demonstration purposes, we model the contaminant molecules by a single spherical site (denoted as a D site) having the same Lennard-Jones parameters as a C site. The bulk mixture of polymer (A, B, C sites) and contaminant (D site) was treated with PRISM theory to calculate the 10 partial structure factors involving the various pairs of sites. As before, the structure factor matrix $\hat{S}_{\alpha\gamma}(\mathbf{k})$ is then used as input to the Wall PRISM equations (14) and (16). The resulting wall profiles are shown in Figure 6. The parameters used in these calculations are given in Table 1.

It can be seen from this figure that the contaminant (D sites) are present at the wall in a much higher concentration than they are in the bulk polymer far from the wall. The absolute concentration of contaminant is still small since the contaminant only constitutes 2% of the bulk density. Nevertheless, the presence of the D sites at the surface has the effect of displacing the polymer from the surface. This can be seen by comparing the clean surface in Figure 5 with the contaminated surface in Figure 6. Perceptible changes can be seen in the A, B, and C site distributions between the two surfaces. For example, the relative concentration of methyl groups (C sites) dropped from 3.6 to 3.3 because of the contamination.

Figure 6 - Wall PRISM Predictions for PDMS Near a Neutral Surface in the Presence of 2% by Volume of Single Site Contaminant Denoted as D. $g_w(z)$ is the site density, normalized by the bulk density, of sites of type A, B, C, or D.

The overall effect of the 2% contamination on the total concentration of polymer near the wall is shown in Figure 7.

Figure 7 - A Comparison Between the Average Polymer Density Profile Between Clean and Contaminated Surfaces.

Table 1 - Lennard-Jones parameters used in the PRISM and Wall PRISM calculations.

Parameter	Site A	Site B	Site C	Site D
σ (Å)	3.033	3.804	3.93	3.93
ϵ (cal/mol)	95.7	31.0	156	156

Since the contaminant contributes nothing to the strength of the adhesive bond, the bond strength will be lower for the contaminated surface because the polymer concentration near the surface is diminished. We can estimate the effect of the contamination on the bond strength by examining its effect on the work of adhesion. Neglecting the entropic contribution, we estimate the work of adhesion W_s per unit area as

$$W_s = \sum_{i=A,BC} \int_0^{\infty} v_i(z) \rho_i(z) dz \quad (17)$$

where $v_i(z)$ is the interaction potential between site i and the substrate and $\rho_i(z)$ is the corresponding density profile. The wall potential can be approximated by a 9/3 potential¹⁶

$$v_i(z) = K\sqrt{\epsilon_i} \left[\frac{2}{15} \left(\frac{z}{\sigma_i} + 0.8584 \right)^{-9} - \left(\frac{z}{\sigma_i} + 0.8584 \right)^{-3} \right] \quad (18)$$

obtained by integrating the conventional Lennard-Jones potential over the x and y directions. K is a system specific parameter defined by

$$K = \frac{2\pi\rho_s}{3} \left(\frac{\sigma_s + \sigma_p}{2} \right)^3 \sqrt{\epsilon_s} \quad (19)$$

where ρ_s is the substrate density, σ_s is the Lennard-Jones σ -parameter for a surface atom, and σ_p is the average σ -parameter for the polymer sites. For a PDMS substrate we estimate K to be approximately $44.1 \text{ (cal/mol)}^{1/2}$ using the Lennard-Jones parameters in Table 1.

In Eq. (17) the $\rho_i(z)$ term is the site distribution of the polymer near the substrate and was found from the wall PRISM calculations depicted in Table 1 and Figure 6. From the data in for the clean surface we performed the calculation in Eq. (17) to obtain $W_s=0.038 \text{ J/m}^2$. This is in reasonable agreement with the work of adhesion measured from JKR measurements by Emerson and others of about 0.044 J/m^2 for PDMS against a PDMS substrate (see the section “Contact Mechanics Characterization of the Contaminated Interface” in this report). We can also estimate the effect of contamination by performing the same calculation using the density profiles in Figure 6 which gives $W_s=0.034 \text{ J/m}^2$. Thus in this example, a 2% level of contamination resulted in a 10.5% reduction in the work of adhesion.

In the Wall PRISM calculations presented here, we modeled an idealized system that only used repulsive interactions between polymer sites and between polymer sites and the substrate. Attractive interactions, however, can influence the density profiles. Previous experience with Wall PRISM theory suggests that Wall PRISM theory works best on purely repulsive systems. For this reason, attractive interactions can probably best be handled using the density functional theory methods discussed in the next section.

DENSITY FUNCTIONAL THEORY

In the density functional theory (DFT) of Chandler, McCoy and Singer¹⁷, the free energy of the inhomogeneous system, i.e., a polymer near a wall, is expanded in a Taylor series to second order about the homogeneous bulk system. To help cancel out the higher order terms neglected in the expansion, the free energy of an ideal or reference system is subtracted. An external field is envisioned to act on the ideal system to force the ideal density profile to be the same as the profile of the real system. This ideal field is determined by minimizing the free energy with respect to the density profile. The excess Helmholtz free energy of the inhomogeneous system, $A-A_0$ where the “0” indicates the ideal system, is expanded through second order about the bulk, homogeneous system as²

$$\begin{aligned}
(A - A_0) = & (A - A_0)_{\text{bulk}} + \sum_i \int_V d\mathbf{r} \left[\psi_i(\mathbf{r}) - \psi_i^0(\mathbf{r}) \right]_{\text{bulk}} \Delta \rho_i(\mathbf{r}) \\
& + \frac{1}{2} \sum_{i,j} \iint_V d\mathbf{r} d\mathbf{r}' \left. \frac{\delta^2 (A - A_0)}{\delta \rho_i(\mathbf{r}) \delta \rho_j(\mathbf{r}')} \right|_{\text{bulk}} \Delta \rho_i(\mathbf{r}) \Delta \rho_j(\mathbf{r}')
\end{aligned} \tag{20}$$

where the conjugate variable to the density, $\rho_i(\mathbf{r})$, is the “external field” or “spatially varying chemical potential”, $\psi_i(\mathbf{r}) = \mu_i - U_i(\mathbf{r})$; μ_i is the chemical potential; and $U_i(\mathbf{r})$, the external field. The sums are over site type, and the integrals, over the system volume. The coefficients in the functional expansion are evaluated in the bulk state; and the expansion variables, $\Delta \rho_i(\mathbf{r})$, equal $\rho_i(\mathbf{r}) - \rho_{i,\text{bulk}}$. The thermodynamic identity

$$\psi_i(\mathbf{r}) = \frac{\delta A}{\delta \rho_i(\mathbf{r})} \tag{21}$$

was used to simplify the first order term.

In applications, the fields, $\psi_i(\mathbf{r})$, rather than the densities are the independent variables. As a result, it is more convenient to work in terms of the grand potential functional, W , which is found from the Legendre transform:

$$W = A - \sum_i \int_V d\mathbf{r} \psi_i(\mathbf{r}) \rho_i(\mathbf{r}) \tag{22}$$

This, combined with equation (21), results in

$$\begin{aligned}
\Delta W = & \Delta W_0 - \sum_i \int_V d\mathbf{r} \left[\psi_i(\mathbf{r}) - \psi_{i,\text{bulk}} \right] \rho_i(\mathbf{r}) \\
& + \sum_i \int_V d\mathbf{r} \left[\psi_i^0(\mathbf{r}) - \psi_{i,\text{bulk}}^0 \right] \rho_i(\mathbf{r}) \\
& - \frac{1}{2} \sum_{i,j} \iint_V d\mathbf{r} d\mathbf{r}' C(\mathbf{r} - \mathbf{r}') \Delta \rho_i(\mathbf{r}) \Delta \rho_j(\mathbf{r}')
\end{aligned} \tag{23}$$

where the $\Delta W = W - W_{\text{bulk}}$ and $C(\mathbf{r})$ is the direct correlation function for the bulk polymer far from the substrate. Eq. (23) is general in the sense that an ideal system has not yet been defined. For our purposes, we choose the ideal system to consist of noninteracting chains in the presence of a substrate. If we now minimize the grand potential free energy in Eq. (23) with respect to the density profile,

$$\frac{\delta \Delta W}{\delta \rho(r)} = 0 \quad (24)$$

we obtain the following expression for the ideal external field U_i^0 that forces the ideal chain system to have the same wall profile as the full, interacting chain system:

$$\beta U_i^0(r) = \beta U_i(r) - \sum_j \int_V d\mathbf{r}' C_{ij}(r-r') \Delta \rho_j(r') \quad (25)$$

The functions $C_{ij}(r)$ correspond to the direct correlation functions for the bulk polymer and can be evaluated using PRISM theory. The external ideal field in Eq. (25) can then be used with the ideal chain model (a noninteracting chain) to determine the wall profile. This can be conveniently calculated from a Monte Carlo calculation of a single chain interacting with a wall with the potential $U_i^0(z)$. Thus the difficult, many-chain simulation required in a full simulation is replaced, using DFT, by a much simpler single chain simulation.

A comparison between the DFT theory outlined here and the full simulations of Yethiraj¹ are shown in Figure 8 for 20-site freely jointed chains.

Figure 8 - A Comparison Between DFT Theory (Lines) and Full Many-Chain Monte Carlo Simulations of Yethiraj for Freely Jointed Chain Liquids at Various Packing Fractions η .

It can be seen from Figure 8 that excellent agreement exists between theory and computer simulation on these idealized freely jointed chain liquids. We have also performed DFT calculations on atomistic models. In Figure 9, we show our DFT prediction for PDMS liquids near a neutral surface. It can be seen that there is qualitative agreement between the DFT results in Figure 9 and the corresponding Wall PRISM profiles for PDMS in Figure 5.

At this point, no additional DFT calculations have been performed. Nevertheless, we anticipate that the DFT formalism outlined here could be used to perform contaminant calculations in the same manner as those shown using Wall PRISM theory. However, because DFT has been shown to be a much more accurate theory than Wall PRISM, especially when intermolecular and wall attractions are present, we anticipate that it could be a powerful tool in modeling contamination of surfaces.

Figure 9 - DFT Calculation for PDMS Near a Neutral Substrate.

CLEANING CHARACTERIZATION FOR THE ADHESIVE BOND

INTRODUCTION TO CLEANING

Understanding the fundamental question of “how clean is clean?” is of importance when trying to link surface preparation to adhesion. The objective of this study was to determine the cleanliness levels and corresponding bond strengths after precleaning and after deposition of a hydrocarbon (hexadecane) contaminant. This section focuses on the cleaning aspects and deposition processes utilized to prepare surfaces before bonding. Two different types of cleaners

were used for precleaning purposes. A commonly used hydrocarbon solvent trichloroethylene (TCE) and an aqueous alkaline cleaner Brulin 815GD (Brulin). In previous studies, Brulin has proven to be an effective cleaner for removing organic types of contamination, i.e., Brulin cleaned as well as or better than traditional cleaners TCE, methylene chloride and 1,1,1 trichloroethane¹⁸. Three methods, including Goniometer/Contact Angle, MESERAN, and Auger Electron Spectroscopy (AES), were used to determine cleanliness levels after precleaning. Deposition of a hexadecane contaminant was achieved by means of a low temperature evaporation method. Quantification of the deposited contaminant was attempted with atomic force microscopy (AFM), ellipsometry, and time-of-flight secondary ion mass spectroscopy (TOF SIMS). Aluminum (6061) butt tensile plugs, aluminum plates, and double cantilever beam specimens were used to determine bond strengths.

EXPERIMENTAL

Cleaning Procedures

Two procedures were defined for cleaning 6061 aluminum butt tensile plugs, double cantilever beams, and aluminum plates: the Brulin 815GD clean process and the TCE clean process.

Preclean

A preclean procedure was performed before the defined cleaning processes to remove excess blast media from the part so as not to contaminate the subsequent cleaning baths:

1. The parts were ultrasonically cleaned in ambient deionized water (DIW) for 3 to 5 min; they were then rinsed with a hand-held DIW spray for 45 s to 1 min and rinsed with reagent-grade isopropyl alcohol (IPA) for 30 seconds with a final blow dry step using filtered dry nitrogen. The parts were then cleaned with either a Brulin/DIW/IPA or TCE/IPA process.

Defined Cleaning Processes

2. Brulin 815GD clean process:

- a) Ultrasonically clean in a 10%-by-volume Brulin 815GD, 90%-by-volume DIW (typically >16 megohm-cm) solution at 135°F for 5 min (butt tensile plugs and double cantilever beams) or for 10 min (10" square aluminum plates) in station 2 of the Crest In-Line System.
- b) Rinse with ambient DIW using spray nozzles and hand-held spray for 2 to 3 min in station 3 of the Crest In-Line System.
- c) Rinse in cascading 120°F DIW for 5 min in station 4 of the Crest In-Line System.
- d) Rinse in cascading 120°F DIW for 5 min in station 5 of the Crest In-Line System.
- e) Ultrasonically clean/rinse in ambient reagent grade IPA for 30-60 s in Ney ProSONIK ultrasonic cleaner or stir in reagent grade IPA for 30-60 s.
- f) Blow dry with filtered nitrogen.

3. TCE clean process:

- a) Vapor degrease in reagent grade TCE for 2 min.
- b) Rinse in stirred reagent grade IPA bath for 2 min.

- c) Blow dry with filtered nitrogen.

Contaminant and Deposition Methods

Initial experiments focused on the deposition of mineral oil and hexadecane. Mineral oil was eliminated from the study because its composition can vary. Hexadecane was selected because it is easy to model and because it is representative of a contaminant that is often used for lubrication purposes. Four deposition methods were evaluated in an effort to apply a uniform and repeatable contamination. The methods included (1) vapor deposition in a closed equilibrium environment, (2) deposition utilizing a modified mini vapor degreaser, (3) vapor deposition under vacuum, and (4) deposition by dipping.

Based on the results obtained from TOF SIMS, ellipsometry, and AFM, method one (vapor deposition in a closed equilibrium environment) was selected. In this case, samples (including cylindrical aluminum butt-tensile specimens, polished and unpolished aluminum cantilever beams, sputtered aluminum cover slips, and pieces of silicon wafer) were placed into sample holders or cassettes of perfluoroalkoxy (PFA) Teflon so that the cleaned surfaces of interest were facing down. A puddle of anhydrous hexadecane, 99+%, (approximately 50 mL, typically Aldrich product 29,631-7) was poured into the bottom of a clean, dry Pyrex vacuum desiccator, having no grease on the ground-glass rim or top. The holders and cassettes were placed so that the surfaces of interest were between two and five cm above the top surface of the puddle of hexadecane. The top of the desiccator was set in place and the desiccator with the samples within was carefully placed into the chamber of a Thermotron constant temperature-humidity apparatus. The temperature was held at 100°F for 48 h, the humidity was not controlled. After deposition of the hexadecane, the samples were removed from the desiccator and placed into glass Petri dishes with ozone-cleaned aluminum for gettering of contaminants. Thereafter, the samples were used for further analysis or tests.

Analytical Methods Utilized after Precleaning and Deposition

A Rame Hart Model 100/Contact Angle (CA) goniometer was used to determine surface cleanliness. The goniometer test measures the contact (tangent) angle that is formed between a drop of water and its supporting surface. The method is a relative measurement of surface wettability. In general, the cleaner a surface is (with respect to organic contamination), the lower the contact angle measurement will be. The CA is a qualitative test used as an initial screening tool.

A MESERAN (Measurement and Evaluation of Surfaces by Evaporative Rate Analysis) surface analyzer was the second analytical method used for determining cleanliness. It is a quantitative measurement of microorganic residues down to nanogram/cm² levels, which employs a slope technique. The MESERAN is a non-destructive test method available for in-process organic contamination detection and measurement¹⁹. Evaporative rate analysis technology measures the rate of evaporation of a carbon-14-tagged radioactive chemical with a Geiger counter. The

optimal slope of the log count versus time evaporation curve, expressed as a positive integer, is a valid inverse measure of the amount of residue, i.e., the higher the slope, the less the residue²⁰. Calibration curves have been established for common organic contaminants and can be used to convert slope values to contamination levels in ng/cm².

A third method used for determining cleanliness was Auger Electron Spectroscopy (AES). Residual surface contamination on aluminum 6061 was measured by sputter depth profiling with a Physical Electronics scanning Auger instrument. The analysis was done with a 5 keV accelerating voltage and a beam current of approximately 500 nA. Sputtering was done with a rastered 3 keV Xenon ion beam, producing a sputter rate of approximately 140 ± 10 Å/min on a standard SiO₂ specimen. The sputter depth on the depth profile data can be approximated by this rate, but there is variation of sputter rate on the different materials, so the thickness measurements should be used only for comparative purposes. Before profiling each specimen, an AES survey was obtained from the area selected in order to identify the contaminants present. These elements were selected for depth profiling.

The atomic concentrations were determined from tabulated sensitivity values supplied by the instrument manufacturer²¹. These values cannot be considered accurate in absolute value, but can be used for direct comparison of each data set. The AES data for the plots include noise levels, which explains why the contamination level does not go to zero percent after sputtering for some of the reported results. The contaminant was either completely removed or present only below the detectability limits of the AES technique. The detection limit was nominally defined as 1%, although it could be as low as 0.1% for chlorine, to which the AES technique is very sensitive. The limit may be much higher in cases where AES peak overlaps occur. The data were normalized to a total of 100% for each sputter step. In some cases, the values for the contamination may not go to zero percent due to poor removal during sputtering caused by the surface roughness of the part being analyzed. Carbon can go to zero even though oxygen is still detected. This can occur because the AES technique is more sensitive (> 2.0) to oxygen than carbon.

Analytical Methods Used after Deposition of Contaminant

Time of Flight Secondary Ion Mass Spectroscopy (TOF SIMS) was used to determine the uniformity of contaminants deposited and to estimate the thickness of the contaminants. TOF SIMS is a vacuum-based technique that uses an energetic ion beam to sputter atoms and molecules from the surface. When a beam of ions is incident on a solid surface, atoms, ions, and molecular species can be sputtered from the surface. The sputtered ions can be mass-analyzed to determine the atomic composition, chemical information, and the distribution of the species of interest throughout the sample. Elemental depth distributions are obtained by monitoring the elements or molecules of interest as the ion beam sputters away the surface layers of the specimen. Ion images can be acquired by scanning a focused primary ion beam across the sample surface. The use of a high-resolution mass analyzer yields isotopic analysis that can readily distinguish isotopes and molecular ions with nominally the same mass.

TOF SIMS pulses the primary ion beam onto the sample surface. The secondary ions are extracted through an immersion lens and the times for the various mass ions to reach the detector are measured. The entire mass spectrum is measured for each pulse. For typical ion accumulation times of 2 to 5 min, the dose to the sample is approximately 10^{12} ions/cm². This value is well below the static SIMS dose of 10^{13} ions/cm². This capability allows the analysis of monolayer organic and inorganic surface modifications.

Data were obtained from two edges and center of the 6061 aluminum specimens. Three areas were recorded from each of these regions. The ratio of the peak intensity of the molecular ions associated with the contaminant was normalized to the aluminum or silicon intensity. The average and standard deviation were then calculated for each region.

Atomic force microscopy was used to measure the surface roughness of the sample and to determine the distribution of the deposited contaminant. In contact mode, the data are acquired by measuring deflection of a cantilever, which has a tip at the end, continuously touching the surface of the sample. In non-contact mode, the height of the sample is adjusted by means of feedback in order to maintain a constant distance between the tip and the surface of the sample.

Ellipsometry was used to measure the thickness of the films deposited. In general, the ellipsometer can measure film thickness of at least an order of magnitude smaller than those obtainable by other methods, such as interferometry. Ellipsometers are optical instruments, which measure changes in the state of polarization of collimated beams of monochromatic polarized light caused by reflection from the surfaces of substances. Measurement involves irradiating the surface of a sample at a known angle of incidence with a collimated beam of monochromatic light having a known, controllable state of polarization and determining the differences between the states of polarization of the incident and reflected beams. From the measured differences caused by the sample between the states of polarization of the incident and reflected beams, various properties of the reflecting surface can be computed²².

RESULTS AND DISCUSSION

Contact Angle and MESERAN Results

The static contact angle and MESERAN results for the TCE/IPA clean and Brulin 815GD clean are shown in Table 2 and Table 3, respectively. In Table 2, the average contact angle and MESERAN values for the first two sets of as-received 6061 aluminum plugs were $79.8^\circ \pm 19.1$ and $32,438 \text{ ng/cm}^2 \pm 20,751$ respectively. After cleaning with TCE and IPA, the average contact angle was reduced to $63.4^\circ \pm 2.1$; an improvement of 16.4° and the MESERAN contamination level was reduced to $101 \text{ ng/cm}^2 \pm 83$. In Table 3, the average contact angle and MESERAN values in the as-received condition were $77.6^\circ \pm 17.9$ and $20,036 \text{ ng/cm}^2 \pm 22,236$ respectively. A significant improvement in the contact angle ($11.0^\circ \pm 3.1$) was noted after cleaning with Brulin 815GD and the MESERAN contamination level was reduced to $1988 \text{ ng/cm}^2 \pm 297$. Although the MESERAN contamination level was reduced after cleaning with Brulin, the results did not

mirror the contact angle results. Because the Brulin process has microetched the aluminum surface, it is surmised that the resulting rougher surface has affected the MESERAN results. Typically, a smooth surface is preferred when performing MESERAN measurements because a rough surface will have a tendency to retain the C-14/cyclopentane solution, giving misleading results.

Table 2 - As Received and TCE/IPA Clean 32 RMS 6061 Aluminum Plugs Static-Equilibrium Contact Angle and MESERAN Results.

Plug#	As-received Contact Angle	Contact Angle After TCE/IPA Clean	As-received MESERAN Slope Length of 30	Equivalent CL MESERAN ng/cm ²	MESERAN After TCE/IPA Clean Variable Slope	Equivalent CL ng/cm ²
1	93°	61°	317	7909	1663	219
2	79°	62°	175	30,200	2358	4
3	47°	65°	201	20,261	2036	41
4	90°	66°	154	41,687	1859	115
5	90°	63°	128	62,135	1835	124
AVG	79.8	63.4°	195	32,438	1950	101
STD	19.1	2.1	73	20,751	264	83

CL = Contamination Level
ng/cm² = nanograms/centimeter²

Table 3 - As-Received and Brulin 815GD Clean 32 RMS 6061 Aluminum Plugs Static-Equilibrium Contact Angle and MESERAN Results.

Plug#	Contact Angle As-received	Contact Angle After Brulin Clean		MESERAN Slope As-received Slope/30	Equivalent CL ng/cm ²	MESERAN Slope After Brulin Clean Slope/30	Equivalent CL ng/cm ²
1	57°	15°		394	6110	734	1955
2	90°	10°		131	59338	681	2335
3	92°	7°		251	9867	745	1884
4	59°	10°		218	15607	800	1567
5	90°	13°		270	9258	699	2198
AVG	77.6°	11.0°		253	20036	732	1988
STD	17.9	3.1		95	22236	46	297

In comparison to the static contact angle method, advancing-receding (dynamic) contact angles were also determined. The results for TCE/IPA Clean and Brulin 815GD Clean can be seen in Table 4 and Table 5, respectively. In general, if the hysteresis is less than 10° the difference can be attributed to surface roughness. If the hysteresis is greater than 10°, then chemical heterogeneity can be a factor and the difference can be attributed to areas of different surface energies such as a contaminant. In Table 4, the average advancing contact angle obtained for the as-received condition was 78.8° ±4.4 and the average receding contact angle was 23.0° ±8.5, resulting in a hysteresis of 55.8°. After cleaning per the TCE process, the average advancing contact angle was 68.0° ±7.9 and the receding contact angle was 16.2° ±7.5, a resulting hysteresis of 51.8°, indicating only a slight removal of contaminant on the surface. On the other hand, in the second set of five samples (Table 5), the hysteresis obtained for the as-received condition was 59.0° and the hysteresis after cleaning with the Brulin process was 11.2°, indicating a significant improvement in cleaning or removal of aluminum by the Brulin process. In summary, the advancing-receding contact angle method correlated with the results obtained in the static contact angle method.

Table 4 - Advancing-Receding Contact Angles as Received and TCE/IPA Clean 32 RMS 6061 Aluminum Plugs.

Plug#	Advancing Contact Angle As-received	Receding Contact Angle As-received	Hysteresis	Advancing Contact Angle TCE/IPA	Receding Contact Angle TCE/IPA	Hysteresis
1	75°	24°	51°	76°	17°	59°
2	81°	10°	71°	72°	7°	65°
3	74°	16°	58°	55°	10°	45°
4	77°	28°	49°	62°	22°	40°
5	80°	27°	53°	72°	14°	58°
6	86°	33°	53°	71°	27°	44°
AVG	78.8°	23.0°	55.8°	68.0°	16.2°	51.8°
STD	4.4	8.5	8.0	7.9	7.5	10.1

Table 5 - Advancing-Receding Contact Angles As Received and Brulin 815GD Clean 32 RMS 6061 Aluminum Plugs.

Plug#	Advancing Contact Angle As-received	Receding Contact Angle As- received	Hysteresis	Advancing Contact Angle Brulin 815GD Clean	Receding Contact Angle Brulin 815GD Clean	Hysteresis
1	77°	28°	49°	14°	4°	10°
2	78°	11°	67°	17°	5°	12°
3	89°	26°	63°	20°	7°	13°
4	79°	31°	48°	20°	9°	11°
5	81°	16°	65°	21°	9°	12°
6	80°	18°	62°	24°	13°	9°
AVG	80.6°	21.7°	59°	19.3°	7.8°	11.2°
STD	4.3	7.8	8.3°	3.3	3.3	1.5

Auger Electron Spectroscopy Results

The AES results for as-received; cleaned with the Brulin and TCE processes can be seen in Table 6. The average carbon level for as-received 6061 aluminum samples was 9.3 atomic percent while the average residual value for silicon was 1.2 atomic percent. After cleaning with the Brulin process the carbon level was significantly reduced to 2.7 atomic percent and the silicon level doubled to 2.4 atomic percent. The increase in residual silicon can be attributed to one of the constituents (Si) used to formulate Brulin 815GD. The reduction in carbon level (9.3 vs. 5.6 atomic percent) is not as significant for the TCE clean process, however less residual silicon is detected. In some cases, other contaminants such as calcium, sulfur and magnesium were detected but were considered negligible. These results generally correlate with the contact angle results, i.e., there is a significant improvement noted after cleaning per the Brulin process and a slight to moderate improvement after cleaning with the TCE process.

Table 6 - Auger Electron Spectroscopy Results Elemental Composition - Atomic %.

6061 Aluminum Samples	Carbon	Oxygen	Aluminum	Silicon	Calcium
As-recv'd	9.3	10.9	77.5	1.2	-
Brulin 815GD Clean	2.7	7.8	86.6	2.4	-
TCE/IPA Clean	5.6	7.3	83.9	0.8	0.7

TOF SIMS, AFM and Ellipsometry Test Results

In order to determine the saturation point, 6061 aluminum samples were exposed to hexadecane (method 1) for 24 h, 48 h, and 144 h.

TOF SIMS results indicated that it took approximately 48 h for the hexadecane contaminant to saturate or come to equilibrium and the results also indicated that the contaminant was not distributed uniformly. Rather, the results indicate the hexadecane contaminant was distributed over the surface in “island-like” form. The film thickness after 48 h of exposure was estimated to be approximately one monolayer, defined in this study as 15 to 20 Å. Because TOF SIMS is performed in an ultrahigh vacuum environment, concern was expressed that the contaminant may have been partially volatilized before being analyzed.

To address this problem, two other analytical methods (atomic force microscopy and ellipsometry) were evaluated. As mentioned previously, atomic force microscopy measures the surface roughness of the sample and distribution of the contaminant and ellipsometry measures the thickness of the contaminant. Initially a layer of aluminum sputtered onto glass slides was used for this study because both analysis methods require a highly polished surface. In this case, samples were analyzed after a 48-hour closed environment exposure, after exposure to a Vaporette degreaser for 5 and 15 min and after dipping in hexadecane and blowing the visible hexadecane off with nitrogen.

As with the TOF SIMS results, AFM images for the 48-hour hexadecane exposure indicated that the contaminant was in the form of islands or puddles, i.e., the film was not continuous. Evidence of a discontinuous film was further supported through contact angle measurements. An advancing contact angle of $64.7^\circ \pm 1$ and a receding contact angle of $25.8^\circ \pm 0.8$ were obtained for the 48-hour sample. A hysteresis of 38.9° suggested that the hexadecane coating was discontinuous; i.e., if the hysteresis is $< 10^\circ$, it can be attributed to surface roughness, if $> 10^\circ$, then chemical heterogeneity or areas of different surface energies such as a contaminant become a factor.

Initial ellipsometry analysis on an aluminum-sputtered surface after exposure for 48 hours indicated that the contaminant layer thickness was approximately 3046 ± 620 Å. The relevance of the reported value is highly dependent on the optical constants utilized. In addition, for thicknesses over 500 Å one must have knowledge of the order of magnitude of the thickness from sources other than ellipsometry in order to determine the actual thickness. Upon further analysis, a precleaned aluminum-sputtered sample before deposition revealed a surface similar to that observed after deposition of the hexadecane contaminant. In short, the previously reported contaminant thickness may have been nothing more than the surface morphology or inconsistencies in the aluminum sputter process on glass. Note the similarities in images 1 and 2 in Figure 10 and Figure 11. On the other hand, another attempt to coat and measure the thickness of the contaminant on aluminum coated cover slips (48 hour exposure) reported ellipsometer values between 16.8 Å and 21.6 Å. These values concur with those reported using TOF SIMS. Atomic force microscopy showed inconclusive evidence about the existence of a monolayer of hexadecane on the aluminum.

Figure 10 - AFM Image of Surface of 2000 Å Layer of Aluminum Glass Cover Slip.

Figure 11 - AFM Image of Aluminum Surface After Deposition of Hexadecane.

In order to obtain a uniform initial starting condition, silicon substrates were substituted for aluminum-sputtered samples. An AFM image of a precleaned silicon substrate reveals a uniform surface and is seen in Figure 12. A TOF-SIMS analysis of a silicon surface after cleaning with the Brulin process and analysis after deposition of the hexadecane contaminant can be seen in Table 7. The data are reported as the ratio of peak intensity of the molecular ions associated with the hydrocarbon contaminant (presumably hexadecane fragments) normalized to silicon or aluminum. For example, silicon substrates that were cleaned with the Brulin process gave initial peak intensity values of 0.0600 for the C_3H_5 fragment, 0.0500 for the C_3H_7 fragment, 0.0240 for the C_4H_7 fragment, and 0.0410 for the C_4H_9 fragment. The peak intensities for the silicon substrates after the Brulin cleaning process and deposition of the hexadecane contaminant gave values of 0.0692, 0.0385, 0.0263, and 0.0432 respectively. In this case, the differences before and after deposition are considered noise level and are not necessarily indicative of a monolayer of contaminant. On the other hand, the values reported for the silicon samples that had been cleaned with the Brulin process were suspect; i.e., at the time these samples were processed the purity of the deionized water used to make-up the 10% by volume Brulin solution and to rinse after cleaning may have been contaminated. Typically, the sensitivity of aluminum versus silicon is a factor of two and not a factor of four to six as is indicated in the precleaned (aluminum vs. silicon) control samples.

Figure 12 - AFM Image of a Polished Silicon Wafer Substrate after UV Ozone Clean.

Table 7 - Time of Flight SIMS Data Relative Peak Intensities.

Sample Condition	C ₃ H ₅ Fragment	C ₃ H ₇ Fragment	C ₄ H ₇ Fragment	C ₄ H ₉ Fragment
TCE Clean (Al)	0.0270	0.0200	0.0100	0.0120
Brulin Clean (Al)	0.0146	0.0085	0.0054	0.0060
Brulin + Hexadecane (Al)	0.0444	0.0342	0.0178	0.0250
Brulin Clean (Si)	0.0600	0.0500	0.0240	0.0410
Brulin Clean + Hexadecane (Si)	0.0692	0.0385	0.0263	0.0432
TCE Clean + Hexadecane + Bond (Al Cantilever Beam #4-hex-1)	0.1090	0.0850	0.0534	0.0461
TCE Clean + Hexadecane + Bond (Al Cantilever Beam #4-hex-3)	0.0940	0.0770	0.0448	0.0370

In addition to the silicon results, data for aluminum sputtered samples are depicted in Table 7. The peak intensities for aluminum samples cleaned with the Brulin process gave peak intensity values of 0.0146 for the C₃H₅ fragment, 0.0085 for the C₃H₇ fragment, 0.0054 for the C₄H₇ fragment, and 0.0060 for the C₄H₉ fragment. The peak intensities after Brulin clean and deposition of the hexadecane contaminant gave peak intensity values of 0.0444, 0.0342, 0.0178, and 0.0250 for the C₃H₅ fragment, C₃H₇ fragment, C₄H₇ fragment, and C₄H₉ fragment respectively. The increases in peak intensity are between 3 to 4 times greater than the preclean values and are indicative of approximately one monolayer, determined by TOF-SIMS sputter depth profiling. A post mortem analysis of two cantilever beam specimens that had been cleaned with the TCE process, contaminated with hexadecane and tested for bond strength were also analyzed. As compared to the aluminum preclean controls, the results indicate up to 4 times more hexadecane or other contaminants on the surface.

SUMMARY

Several analytical methods (including contact angle, MESERAN, and AES) were utilized to determine cleanliness levels before and after deposition of a hexadecane hydrocarbon contaminant. The results indicate that the cleanliness levels were significantly improved after cleaning with the Brulin 815GD process and slightly to moderately improved after cleaning with the TCE process. Attempts were made to quantify the uniformity and thickness of the hexadecane contaminant after an evaporation deposition method. Utilizing analytical methods such as TOF SIMS, ellipsometry, and AFM, it appears that the hexadecane contaminant is not uniform but is distributed in "island-like" form and the corresponding thickness is one monolayer or approximately 15 to 20 Å.

With respect to bond strength (as reported in the next section, titled “Fracture Mechanics Characterization of the Interface”), the measurable effect between the Brulin process and the TCE process is modest at best and the measurable effect after hexadecane deposition is none.

FUTURE STUDIES

More recently, a literature search has identified parylene ($C_{20}H_{12}$), a polycyclic aromatic compound, as a molecule that can be deposited as a monolayer under high or ultra-high vacuum conditions onto substrates or surfaces of interest. This material may be superior to hexadecane in future studies, since it is a solid at room temperature and thus less mobile and less volatile, while at the same time not forming chemical bonds to the surface of metals, glass or silicon. Subsequent experiments could show that it is also removable by means of a simple surface cleaning technique, such as vaporous trichloroethylene or the Brulin process. In addition, this molecule can be modeled by computer programs, which simulate the behavior of thin films of polymeric materials on surfaces²³.

FRACTURE MECHANICS CHARACTERIZATION OF THE INTERFACE

Two different fracture mechanics approaches have been used to determine how surface roughness, cleaning method, and contamination affect interface performance. The intent is to use these techniques to explore the interface. One approach characterizes fracture initiation from a sharp corner. Initiation occurs at a critical value of the interface corner stress intensity factor K_a , and this critical value is referred to as the interface corner toughness K_{ac} . The other approach characterizes when an existing interfacial crack will advance. Propagation occurs at a critical value of the energy release rate for crack extension G , and this mixity dependent critical value is referred to as the interfacial toughness $G_c(\psi)$. Note that mixity ψ is a measure of the ratio of shear to normal stresses ahead of the crack tip. The two approaches are complementary, but the measured toughness properties are not directly related. One is associated with fracture initiation at a sharp corner with no reference to a preexisting crack, while the other is associated with the advance of an existing crack. These macroscopic toughness properties were measured using specially designed joints fabricated by bonding aluminum adherends together with a thin epoxy adhesive layer.

FRACTURE MECHANICS TECHNIQUES

The analysis of fracture initiating from a sharp corner is based upon the fact that K_a characterizes the magnitude of the stress state in the region of the interface corner (i.e., the point where the interface intersects the stress-free edge). It is reasonable to hypothesize that failure occurs at a critical K_a value, K_{ac} . See Reedy²⁴⁻²⁶ and Reedy and Guess²⁷⁻³¹ for a detailed discussion of the underlying theory and its application. This approach is analogous to linear elastic fracture mechanics, except here the critical value of the stress intensity factor is associated with a discontinuity other than a crack. In the present study, K_{ac} was determined by measuring the strength of tensile loaded, cylindrical butt joints formed by bonding two 6061 T6 aluminum rods

together with a thin epoxy adhesive bond. Specimens with different bond thickness were tested with the nominal bond thickness ranging from 0.25 to 2.00 mm. The adherends are solid cylinders (28.6 mm diameter by 38.1 mm long) that have been precision machined to guarantee the ends are flat and perpendicular to the cylinder axis, and the edges are left sharp. The adherends were attached via a threaded connection to the load train using a chain linkage. All specimens were loaded at a crosshead displacement rate of 0.2 mm/s.

The relationship between butt joint strength and K_{ac} is

$$K_{ac} = 0.544\bar{\sigma}h^{0.268} \quad (26)$$

where $\bar{\sigma}$ equals the nominal applied tensile stress at joint failure and h equals one half of the bond thickness. Eq. (26) assumes that the epoxy adhesive has a Young's modulus of 3.5 GPa and a Poisson's ratio of 0.35, and that the adhesive bond is thin when compared to all other joint dimensions. Note that when the K_{ac} failure criterion is applicable (i.e., small-scale yielding conditions apply) the log of joint strength varies linearly with the log of bond thickness, and a change in the K_{ac} value causes the plotted line to shift parallel to itself (see Eq. (26)). There is convincing evidence that the K_{ac} fracture criterion can be used to predict failure. Reedy and Guess²⁷⁻³¹ have shown that the observed reduction in the tensile strength of adhesively bonded, cylindrical butt joints with increasing bond thickness as well as the dependence of this relationship on adherend stiffness is accurately predicted by a K_{ac} criterion.

Interfacial toughness is a macro-scale material property that characterizes when an existing interfacial crack will advance. A detailed discussion of interfacial fracture mechanics theory is found in Rice³², Hutchinson, and Suo³³. One aspect of interfacial fracture mechanics that distinguishes it from traditional linear elastic fracture mechanics is the role of mode mixity. Asymmetries with respect to the interface are responsible for the inherently mixed mode condition found at the tip of an interfacial crack. Both normal and shear stresses are present on the interface ahead of the crack tip, and in general, the ratio of these stresses changes with distance from the crack tip. The level of mode mixity (defined as the arctangent of the ratio of shear stress to normal stress at a fixed distance $\hat{l}$ in front of the crack tip in the region dominated by the stress singularity) depends on the elastic properties and the body's overall geometry and loading. According to current thought, resistance to interfacial crack propagation is most conveniently specified in terms of critical energy release rate G_c versus the mode mixity $\hat{\psi}$. The fracture criterion for interfacial cracking is then defined by

$$G = G_c(\hat{\psi}) \quad (27)$$

where $G_c(\hat{\psi})$ is the mode mixity dependent interfacial toughness. An interface crack that is subjected to mode mixity $\hat{\psi}$ advances when the energy release rate for crack extension G equals the critical value associated with that mode mixity, $G_c(\hat{\psi})$. There is experimental evidence^{34,35} at least for relatively weak interfaces, that G_c increases substantially with increasing $\hat{\psi}$.

In the present study, the sandwiched asymmetric double cantilevered beam³⁶ (ADCB) was used to measure G_c . The sandwiched ADCB specimen bonds two aluminum beams of differing thickness together with a thin epoxy layer. The specific test geometry used bonds of 4.6 and 9.1 mm thick beams together with a thin adhesive layer (both beams are 12.7 mm deep and 120 mm long). Specimens with different bond thickness were tested with a nominal bond thicknesses of either 0.5 or 1.0 mm. The specimen is pinned into a load train that utilizes a chain linkage and is loaded by pulling the ends apart at a crosshead displacement rate of 1.0 mm/s to propagate a crack along the interface with the thinner beam. The crack grows stably with increasing end displacement allowing several G_c measurements to be made while testing a single specimen. G_c depends on the load to propagate a previously arrested crack and the associated crack length (inferred from the measured specimen compliance). The calibration used to determine G_c from the measured load and crack length is based upon results published by Bao et al.³⁷ for a single material DCB. A finite element analysis indicates that their results can be applied to the present sandwiched ADCB if plane strain G is scaled by a factor of 1.03 while the associated plane stress specimen compliance is scaled by 0.95. The finite element analysis also indicates that this specimen has a mode mixity of $\psi_{r=0.01 \text{ mm}}$ of about -10° .

SPECIMEN FABRICATION

Four sets of butt joints and four sets of sandwiched ADCB specimens were tested in order to evaluate the effect of surface roughness, cleaning method, and contamination on interface performance. The butt joints were assembled in a V-block fixture to ensure alignment of the two adherends, and a RTV boot was used to hold the epoxy resin in the bond gap during cure. The RTV boot contains an injection hole and a reservoir to accommodate epoxy shrinkage. The ADCB specimens were fabricated in an open cavity RTV mold that confines the epoxy. The thinner adherend is placed at the bottom of the cavity. Small spacers are bonded to the ends of this adherend to define the epoxy layer thickness, and the thicker adherend is then positioned on top. The upper adherend contains through the thickness injection and exit holes for the epoxy. These holes are at opposite ends of the adherend. After the epoxy is injected, the mold is placed in an oven to cure the epoxy. The epoxy adhesive is an Epon 828 resin (Shell) crosslinked with Jeffamine T-403 (Huntsman Chemical Co.) at a 100:43 weight ratio. All four sets of ADCB specimens and one set of the butt joints were cured for 24 hours at 50°C followed by an additional 24 hours at 40°C. This cure schedule was chosen to minimize residual stress. The epoxy's glass transition temperature is 68°C (dielectric measurement technique). Three sets of the butt joints added an initial 24 hours at 28°C step to the cure schedule to simplify handling. This modification of the cure schedule has minimal effect on the epoxy's properties. Compression tests of molded epoxy plugs cured with and without the 28°C step yielded nearly identical stress-strain relations. Joints with a range of bond thickness were fabricated to examine the effect of this parameter. Note that when the K_{ac} failure criteria hold, K_{ac} should not depend on bond thickness. Likewise when interfacial fracture mechanics applies, $G_c(\psi)$ should not depend on bond thickness.

The aluminum bonding surfaces of most joints were lightly sandblasted (60 grit alumina oxide), although the surfaces of some joints were left in the as-machined condition where still others were polished with 6 μm grit to assess the effect of surface roughness. The root mean square roughness, R_q , of the surfaces was measured with a noncontact, optical probe (R_q is defined in Surface Texture ASME B46.1-1995). A long wavelength cutoff of 0.8 mm was used for as-machined butt joint surfaces, whereas a cutoff of 2.5 mm was used for all other surfaces. The adherends were cleaned just prior to bonding. An aqueous alkaline solution (Brulin 815 GD) was used in most cases, although some plugs were solvent cleaned (trichloroethylene) to assess the effect of the method of cleaning. To study the effect of contamination, hexadecane was deposited on the surfaces of a small number of samples. The following procedure was used to apply the hexadecane coating. First the surfaces were cleaned, and then the samples were placed into perfluoroalkoxy (PFA) Teflon sample holders. A puddle of anhydrous hexadecane, 99+% was poured into the bottom of a clean, dry glass vacuum desiccator. The surfaces were positioned between two and five centimeters above the top of the puddle of hexadecane. The desiccator was closed and placed within a constant temperature-humidity chamber and held at 38°C for 48 hours. After deposition of the hexadecane, the adherends were removed from the desiccator and placed into glass Petri dishes with ozone-cleaned aluminum for gettering of contaminants until they were used to fabricate ADCB and butt joint specimens. Table 8 lists fabrication parameters for the four sets of butt joints while Table 9 lists fabrication parameters for the four sets of ADCB specimens.

Table 8 - Fabrication Parameters for the Four Sets of Butt Joints.

Set	Surface Roughness R_q (μm)	Cleaning Method	Cure Cycle ¹ (°C)	Bond Thickness (mm)	Number Joints
1	1	Aqueous Alkaline	50/40	0.2/0.5/1.0	27
	5			0.5	9
2	1	Aqueous Alkaline	28/50/40	0.3/0.5/1.0	20
	5			0.5	7
3	5	Aqueous Alkaline	28/50/40	0.3/0.5/1.0	12
	5	Solvent		0.3/0.5/1.0	12
4	4	Aqueous Alkaline	28/50/40	0.3/0.5/1.0	8
	4	Aqueous Alkaline then contaminated with hexadecane		0.5	3

¹ Held 24 hours at each temperature.

Table 9 - Fabrication Parameters for the Four Sets of ADCB Specimens.

Set	Surface Roughness R _q (μm)	Cleaning Method	Cure Cycle ¹ (°C)	Bond Thickness (mm)	Number Specimens
1	1	Aqueous Alkaline	50/40	0.6/1.2	10
	5			0.6/1.2	10
2	1	Solvent	50/40	0.6/1.1	4
	5			0.6/1.1	4
3	0.1	Aqueous Alkaline	50/40	0.5	2
	7				2
	0.1	Solvent		0.5	2
	7				2
4	0.1	Solvent	50/40	0.5	3
	0.1	Solvent then contaminated with hexadecane		0.5	3

¹ Held 24 hours at each temperature.

SENSITIVITY OF K_{AC} AND G_C TO SURFACE PREPARATION

Table 10 reports the K_{ac} data measured using the butt joint specimens while Table 11 reports the G_c data measured using the sandwiched ADCB specimens. All tests were run at room temperature. A fractography examination of the failed butt joints found that failure always initiates adhesively along a segment of the specimen periphery (i.e., at low magnification the initial failure zone appears to be interfacial). Beyond this thumbnail-like region, the failure is cohesive. A visual examination of the failed ADCB specimens reveals that the crack runs along the interface and there is no indication of cohesive failure.

Table 10 - Sensitivity of K_{ac} to Surface Preparation.

Set	Cleaning Method	Surface Roughness R_q (μm)	Joints Tested	K_{ac} ($\text{MPa mm}^{0.27}$)	Standard Deviation ($\text{MPa mm}^{0.27}$)
1	Aqueous Alkaline	1	27	12.9	1.1
	Aqueous Alkaline	5	9	17.6	1.7
2	Aqueous Alkaline	1	20	8.0	0.7
	Aqueous Alkaline	5	7	14.9	0.9
3	Aqueous Alkaline	5	12	16.9	1.3
	Solvent	5	12	14.9	1.1
4	Aqueous Alkaline	4	8	15.4	1.8
	Aqueous Alkaline then coated with Hexadecane	4	3	16.0	1.2

Table 11 - Sensitivity of G_c to surface preparation.

Set	Cleaning Method	Surface Roughness R_q (μm)	Data Points	G_c (J/m^2)	Standard Deviation (J/m^2)
1	Aqueous Alkaline	1	29	31	7
	Aqueous Alkaline	5	51	126	11
2	Solvent	1	18	16	4
	Solvent	5	31	84	7
3	Aqueous Alkaline	0.1	14	22	3
		7	18	168	5
	Solvent	0.1	14	16	3
		7	21	147	6
4	Solvent	0.1	14	11	3
	Solvent then coated with Hexadecane	0.1	14	10	1

Interface corner toughness K_{ac} is clearly dependent on surface roughness (Table 10). Both Set 1 and Set 2 contain joints with sandblasted ($R_q = 5 \mu\text{m}$) and as machined ($R_q = 1 \mu\text{m}$) surfaces. The measured K_{ac} of Set 1 joints increased 36 percent when the as-machined surface is sandblasted. Set 2 joints show an even greater increase in K_{ac} (86 percent). It should be noted that although the as-machined surfaces of the Set 1 and Set 2 adherends have similar R_q values, the nature of the roughness is quite different. Set 1 plugs contain several sets of straight, parallel grooves. Each set of grooves covers the entire surface, but each set is rotated with respect to the others. The machining marks on Set 2 are concentric circles overlaid with short, arc-like scratches. The method used to clean the bonded surfaces appears to have at most a modest effect. Set 3 samples

cleaned with an aqueous alkaline solution had $K_{ac}=16.9 \text{ MPa mm}^{0.27}$ while those with a solvent had $K_{ac}=14.9 \text{ MPa mm}^{0.27}$. The deposition of a small amount of hexadecane onto the surface prior to bonding had no measurable effect (Set 4). Apparently, the hexadecane is either swept away during the injection of the epoxy resin during fabrication, the hexadecane diffuses into the epoxy, or the effect is minimal compared to the adhesion effects.

The interfacial toughness G_c shows the same dependencies as K_{ac} . G_c is clearly a strong function of surface roughness. Sets 1 and 2 data show that G_c increases by more than a factor of four as R_q varies from 1 to 5 μm . The method used to clean the bonded surfaces again appears to have at most a modest effect. Consider the Set 3 samples with the rougher surface ($R_q=7 \mu\text{m}$). Those cleaned with an aqueous alkaline solution have a 14 per cent higher G_c than that of samples cleaned with a solvent. As in the butt joint tests, the deposition of a small amount of hexadecane onto a surface before bonding had no measurable effect (Set 4).

CONTACT MECHANICS CHARACTERIZATION OF THE CONTAMINATED INTERFACE

We are particularly interested in using the work of adhesion measurements as a means to facilitate our understanding of the adhesive failure mechanisms for systems containing encapsulated and bonded components. Of the several issues under investigation, one is the effect of organic contamination on the adhesive strength for several types of polymer/metal interface combinations. The specific question that we are trying to address is at what level of contamination does adhesive strength decrease. The use of contact mechanics, the JKR method, is a good approach for studying this question. Another approach being studied is the use of interfacial fracture mechanics as discussed in the previous section, "Fracture Mechanics Characterization of the Interface." The model contaminant is hexadecane, a non-polar, medium molecular weight hydrocarbon fluid. We choose hexadecane because it replicates typical machining fluids, is nonreactive with Aluminum (Al) surfaces, and should not dissolve readily into the adhesive systems of interest. The application of a uniform, controllable and reproducible hexadecane layer on Al surfaces has proven to be difficult as discussed in the section titled "Cleaning Characterization for the Adhesive Bond." A primary concern is whether studies of model systems can be extended to systems of technological interest.

The JKR theory is a continuum mechanics model of the contact for two solid spheres that was developed by Johnson, Kendall and Roberts³⁸ (JKR). The JKR theory is an extension of Hertzian contact theory³⁹ and attributes the additional increase in the contact area between two soft elastomeric spheres to adhesive forces between the two surfaces. The JKR theory allows a direct estimate of the surface free energy of solids as well as the work of adhesion between solids.

The so-called JKR apparatus is now widely used by a number of researchers to examine adhesion forces between solid surfaces. However, several authors have reported significant adhesion hysteresis that is not predicted by the JKR theory. For example, Silberzan⁴⁰ and Choi⁴¹

have used the JKR method to study the self-adhesion hysteresis in extracted siloxane elastomers. Silberzan⁴⁰ observed a significant hysteresis upon the unloading of two siloxane hemispheres that had been extracted in chloroform and dried under vacuum. The extraction material was 7-9% by weight. In a similar study, Choi⁴¹ observed self-adhesion hysteresis between siloxane hemispheres extracted with toluene and dried under vacuum. The amount of extracted material was shown to be a function of the crosslinker-to-PDMS ratio and also correlated with the amount of hysteresis. Hysteresis has also been observed in our laboratory⁴², although the cause was attributed to the additives used in commercial PDMS systems.

EXPERIMENTAL

PDMS Synthesis

Model networks of poly(dimethylsiloxane) were synthesized by reacting vinyl-capped poly(dimethylsiloxane) with tetrakis(dimethylsiloxy)silane in the presence of a platinum catalyst. The use of the platinum - divinyltetramethyldisiloxane complex allowed the polymerization to proceed at room temperature without the formation of by-products. All reactants were used as received from Gelest Inc.

The procedure used to synthesize the PDMS networks is as follows. First, tetrakis(dimethylsiloxy)silane was added using an Eppendorf volumetric dispenser. With the amount of cross-linker fixed, a 0.75 stoichiometric amount of vinyl-capped PDMS (6000 g/mol) was added with a 3 mL syringe. The contents were then mixed thoroughly and stored in a freezer at -20°C. Once the temperature was low enough to slow the reaction, approximately 150 ppm of platinum - divinyltetramethyldisiloxane complex was worked into the system. Hemispheres, which are used as the JKR lens, were prepared using a pipette. Drops of the mixture were placed on tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane treated glass surface. The PDMS hemispheres were treated in the following fashion: Series 1: room temperature cured; Series 2: room temperature cured followed by 1 hour at 150°C (under nitrogen purge); Series 3: same as Series 2 but extracted with toluene for 24 hours followed by drying at room temperature under vacuum; Series 4: same as 3 but exposed to ethylene gas after extraction.

JKR Apparatus

A custom JKR apparatus was built to allow unattended operation after sample insertion. Temperature control is within ± 0.1 °C of the set point. Accurate temperature control has been established for 30 -150 °C. Loading and unloading displacements are adjustable down to 1 μm steps. A schematic of the apparatus is shown in Figure 13. The operation of the instrument is via National Instruments Labview® software. Custom instrument modules, virtual instrument (vi), were written in C++ for the different hardware/software interfaces. Image analysis of the contact area is done Image Pro®. A photograph of the apparatus is shown in Figure 14.

JKR Measurement

One or two hemispherical lenses are mounted into the JKR apparatus. Measurements are made at 30 - 60 %RH. Typically, the loading and unloading measurements under done with an incremental change in displacement of 3 μm per step. Figure 15 shows the schematically how the area changes as a function of load. The work of adhesion was determined by recording the contact radius as a function of contact load and using the JKR equation to fit the data:

$$a^3 = (R/K) \{P + 3\pi WR + [6\pi WRP + (3\pi WR)^2]^{1/2}\} \quad (28)$$

where a is the contact radius, R is the effective radius of the lenses, P is the contact load, and W is the work of adhesion. The technique was calibrated by following the procedure developed by Whitesides' group⁴³. The two hemispheres, approximately 2.2 mm diameter, were compressed (loaded) at 5 μm steps, held for 5 min before recording the force and area. The unloading (tension) data was collected in the same way. Figure 16 shows the hysteric curve for a PDMS sample. The results are consistent with good PDMS samples: little hysteresis is observed, the value of Wa (the product of the contact radius and the work of adhesion) is near 44 and the curve did not cross zero showing nearly idea behavior. Contact angle data correlated with JKR data⁴⁴.

Figure 13 - JKR System Block Schematic.

Figure 14 - Contact Mechanics (JKR) Apparatus.

JKR Measurement Sphere on Plate Interface

Change in Contact Area Due to Increased Load

Figure 15 - Loading of a Hemisphere onto a Flat Surface.

Figure 16 - JKR Results of Two PDMS Hemispheres - $W_a = 44.03$, $K = 6.48 \times 10^5$. (Series 2 hemispheres.)

RESULTS AND DISCUSSION

Previous studies in our laboratory⁴⁴ on PDMS self-adhesion resulted in a work of adhesion of 44.05 mJ/m^2 , which agrees well the surface energy of 22 mJ/m^2 measured on flat surfaces with contact angles of probe liquids. However, further testing on extracted PDMS showed hysteresis⁴⁵. Therefore, the series of treated PDMS lenses were studied in an effort to understand the origin of the hysteresis.

The JKR result for the Series 1 hemispheres is shown in Figure 17. Note the pronounced self-adhesion hysteresis, i.e. the unloading curve does not superimpose on the loading curve. Arguments for hydrogen bonding between Si-OH and entanglements between tethered chains could be used to explain the occurrence of adhesion-hysteresis. Note that the oxidation of Si-H at room temperature seems unlikely.

Figure 17 - JKR Results of Two Non-extracted Room Temperature Cured PDMS Hemispheres - $W_a=44.05$, $K=1.06 \times 10^6$. (Series 1 hemispheres.)

The JKR result for the Series 2 hemispheres was shown in Figure 16. Note the lack of self-adhesion hysteresis, i.e. the unloading curve closely follows the loading curve. The oxidation of Si-H at 150°C could occur since there are excess Si-H groups available, however, these highly polar functional groups would most likely be buried under the low energy surface. The JKR result for the Series 3 hemispheres is shown in Figure 18. Note the pronounced self-adhesion hysteresis observed. Extraction could lead to tethered chains on the PDMS surface and exposure of Si-H groups. The JKR result for the Series 4 hemispheres is shown in Figure 19. Note the presence of hysteresis. Therefore, hysteresis can occur without the presence of Si-H groups and these results support the tethered chain theory proposed by Choi⁴¹. To further understand the adhesion hysteresis phenomenon, the hemispheres were examined under both an optical microscope and SEM. Micrographs before and after extraction by toluene showed the microscopic blemishes on the surface of the PDMS hemispheres. One could postulate that porous interface occurs between the two hemispheres and it is the collapse of the pores that gives rise to the self-adhesion hysteresis.

Figure 18 - JKR Results of Two Extracted Post Cured PDMS Hemispheres - $W_a = 44.01$, $K = 4.91 \times 10^5$. (Series 3 hemispheres.)

Figure 19 - JKR Results of Two Extracted Post Cured PDMS Hemispheres Exposed to C_2H_4 - $W_a = 44.05$, $K = 1.06 \times 10^6$. (Series 4 hemispheres.)

Early studies performed in this laboratory involved the determination of W_a between silicone (PDMS) and Al surfaces in order to establish the potential adhesive failure mechanisms. However, the JKR studies using commercial based PDMS was fraught with difficulty that were attributed to the additives used in commercial PDMS systems. We could not discriminate hydrogen-bonding effects between Al_2O_3 and hydroxyl groups in the PDMS, and other possible bonding mechanisms.

The next effort was to measure the adhesion between PDMS/Al surfaces for contaminated and two cleaning techniques. In studying systems that have strong adhesive forces the curves can be difficult to interpret because of their nonlinearity. Inconsistent JKR data was obtained from Al sputtered samples. We found some form of cleaning was necessary. Rinsing the sputtered Al samples with acetone after deposition left a visible film. Surface analysis of the residue gave inconclusive results. Deploying aggressive cleaning resolved the residue issue and gave consistent results. In Figure 20 a small amount of hysteresis and pull-off force is seen. This is consistent with the increase in surface reactivity from the expected above the sputtered Al after the chromic-sulfuric acid clean. However, in Figure 21 where the surface is contaminated with hexadecane, the large hysteresis and pull-off force were not expected. The surface energy of the PDMS was measured to be 22 mJ m^{-2} and is mostly non polar. Thus the expectation is that the non-polar interactions give a low hysteresis and pull-off force. The results from the plasma-cleaned surface are as expected. In Figure 22 large hysteresis and pull-off forces for the plasma cleaned surface are seen. A substantial decrease with hexadecane contaminate is seen in Figure 23. The results from Figure 22 and Figure 23 are contrary to Figure 20 and Figure 21. The source of this discrepancy is for a future study. In Figure 22 the adhesive strength can be determined from the pull off force from rapid drop off in contact area at constant tensile force.

Figure 20 - Sputtered Al, Cleaned with Chromic-Sulfuric Acid.

Figure 21 - Sputtered Al, Cleaned with Chromic-Sulfuric Acid and Hexadecane Contaminated.

Figure 22 - Sputtered Al Plasma Cleaned.

Figure 23 - Sputtered Al Plasma Cleaned and Hexadecane Contaminated.

SUMMARY

Tools were developed involving the convergence of several expert areas across Sandia that allow for the robust manufacture of bonded structures. These tools include models and test techniques that can be applied to adhesively bonded components (structural joints, weapon sub-assemblies), and to encapsulated components (neutron generators, electronic packaging). Moreover, we increased our fundamental understanding of the effect of known contaminants on the bond interface for both adhesives and encapsulants. However, the complexity of the adhesive phenomena was clearly highlighted.

A simulation modeling technique, polymer reference interaction site model applied near wall (Wall PRISM), provided the capability to include contaminants on the surface. The process requires a molecular description of polymer and contaminates as input and the results are critically dependent on its accuracy. Calculations on the effect of contamination were performed for 1% by weight of ethanol contamination on the structure of a silicone adhesive near a surface. This change in the PDMS structure leads to approximately an 8% reduction in the work of adhesion. The contact mechanics, JKR, studies obtained similar results.

The demonstration of repeatable coatings and quantitative analysis of the surface for deposition of controlled amounts of contamination was based on three deposition methods. Hexadecane and mineral oil contaminants were studied. Although, we clearly demonstrated the difficulty of

creating controlled, repeatable contaminated surfaces. This is a primary reason why traditional cleaning studies focus on relative comparisons.

Failure of the adhesive joint, as studied using fracture toughness studies, was considered as a tool in understanding the adhesive bond. The effect of the cleaning process used on interface toughness was determined by measuring the toughness of an aluminum/epoxy interface for both Brulin and TCE cleaned aluminum surfaces. The toughness was determined using an Asymmetric Double Cantilever Beam (ADCB) specimen. The measured toughness of samples with a Brulin cleaned aluminum surface is slightly greater than that with a TCE cleaned aluminum surface (~15% greater).

The sensitivity of measured fracture toughness to various test conditions to ensure the reliability of the measurement was determined. We found that interfacial toughness (measured using ADCB sample) is a strong function of surface roughness, increasing by about a factor of five as the surface roughness increases from 1 to 5 micron rms. Interface corner toughness, (measured using a butt joint specimen) is also strongly dependent on surface roughness. It is interesting to note that surface roughening is a common technique used by adhesion experts to improve the chances of achieving good adhesion. The dependence of butt joint strength on bond thickness is predictable, and the interface corner toughness is independent of bond thickness. Contamination was not found to have a significant affect at the levels studied here. The possibility of surface roughness dominating contamination affect was considered long before this study started.

The work of adhesion value for silicone/silicone interface was determined by a contact mechanics technique known as the JKR method. These values compare within experimental error with recent theory and other experimental techniques. The interaction between silicone and a clean Al surface shows a dependence on surface roughness and chemical interaction. New silicones were synthesized to study the effect in more detail. Contaminated surfaces with hexadecane could be readily measured by this technique. However, the results were at times ambiguous. Correlation with fracture data has allowed a better understanding between interfacial fracture parameters and surface energy.

Critical program review from outside Sandia was done at a Semiconductor Research Corporation Workshop. Also Ford Research's expert adhesionologist, Ray Dickie reviewed the program. Both reviews provided positive feedback and gave our accomplished work the highest compliments.

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