



Chemical Modification and Attempted Polymerization of Self-Assembled Monolayers of Hexadecanedioic Acid at Aluminum Surfaces

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Abstract

A self-assembled monolayer (SAM) of hexadecanedioic acid (HDDA) was prepared on an aluminum substrate for purposes of preventing or retarding the consequences of atmospheric corrosion. To enhance the protective qualities of the film, a scheme was developed to polymerize the exposed carboxylic acid functional groups, while enhancing the thickness of the film. To accomplish this, an attempt was made to cross-link the HDDA with octyltrichlorosilane (OTS). Subsequent experiments using a perfluorinated carboxylic acid as the base layer suggest that the OTS is aggressive enough toward the aluminum surface to completely remove the underlying organic SAM and displace it with siloxane (Si-O) linkages at the metal surface. Polarization modulated Fourier transform infrared absorption spectroscopy (PM-FTIRRAS) and contact angle measurements confirm the displacement.

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1. Introduction

Experiments show that for certain molecules and substrates, a self-assembly process occurs in which a well-ordered and stable monolayer of the molecules chemisorbed to the surface forms (see Figure 1). These films are similar to Langmuir-Blodgett films, but are formed spontaneously by self-assembly of the molecules from a dilute (usually 5-mM concentration) solution. The most extensively studied of these systems is the combination of alkane thiols, adsorbed to a gold surface, although alkanolic acids on aluminum oxide show similar behavior. Studies indicate that by altering the composition of the chain, in particular its length (n), or the tail-group composition, the characteristics of the surface can be changed (Troughton et al. 1988; Bain and Whitesides 1988). The control of such properties, as wetting and impedance, may offer advantages in the field of corrosion protection.

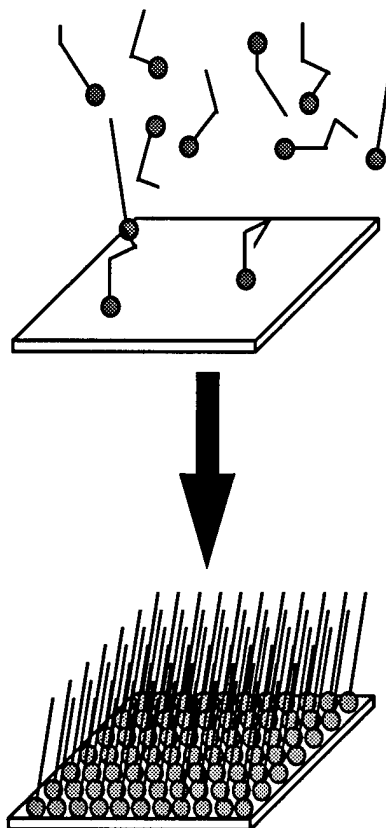


Figure 1. Carboxylic Acids Self-Assembled at Aluminum Oxide Surfaces.

The U.S. Army and the private sector are interested in the development of environmentally friendly protective coatings that are lightweight, removable without volatile organic solvents, and robust under ambient conditions. These coatings could be applied to metal surfaces by immersion and have the advantage of being able to cover rough or irregular surfaces against atmospheric corrosion. One such candidate for this work is carboxylic acid terminated alkane chains that have been found to self-assemble at clean aluminum oxide surfaces (Allara and Nuzzo 1985; Aronoff et al. 1997). These substances may serve as substitutes for primers that currently contain lead and chromate compounds. This work investigates cross-linking the molecules in the self-assembled monolayer (SAM) with a trichlorosilane, thereby simultaneously forming a cross-linked surface and extending the length of the chain and thickness of the film.

2. Experimental

Silicon wafers were purchased from Silicon Sense, Nashua, NH; cleaned in piranha (0.3 parts 30% H₂O₂, and 0.7 parts concentrated H₂SO₄); rinsed; and dried. They were then placed in a vacuum evaporator (10⁻⁶ torr) where they were coated with ~500 Å of pure aluminum. The evaporator was then vented to the atmosphere, which resulted in the formation of a layer of aluminum oxide at the surface. These substrates were then treated by immersion into a solution of 1% acetic acid in dry ethanol. After 24 h, the substrates were examined by a polarization modulated Fourier transform infrared reflectance absorbance spectroscopy (PM-FTIRRAS), using a Mattson Research Series 1 instrument.

Next, all samples were characterized by contact angle measurements using a model VCA 2000 contact angle measurement apparatus. The probe liquid was a single drop of triple distilled water that formed a droplet at the end of a hypodermic needle and was carefully lowered to touch the surface of the substrate. The contact angle reported is the mean value of 10 readings of different droplets on the same sample. The contact angle is reported as angle γ_{SL} (solid-liquid interface) as illustrated in Figure 2.

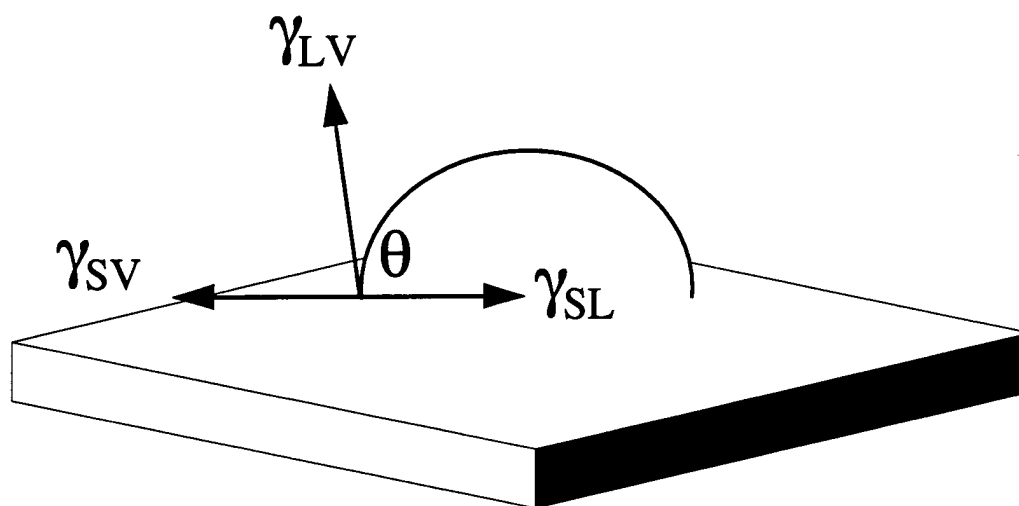


Figure 2. Contact Angle Measurements θ of Distilled Water at SAM Surface.

Sample solutions were prepared by carefully weighing enough hexadecanedioic acid (HDDA) to make a 5-mM solution in dry ethanol. The acid was allowed to dissolve, and the substrates submerged for 4 days.

Infrared spectroscopy is performed by PM-FTIRAS (Green, Barner, and Corn 1991). At a high angle of incidence, the intensity of a reflected p-polarized IR beam is enhanced at a metal surface. In contrast, an s-polarized beam has virtually no intensity at the metal surface. The selection of p-polarized light over s-polarized light has been utilized to obtain the differential reflectance spectrum of the adsorbed surface species, $\Delta R/R$, by polarization modulation of the IR light.

Characterization by PM-FTIRAS (500 scans, resolution 4 cm^{-1}) shows the emergence of peaks that represent methylene stretching vibrations that are characteristic of SAM formation.

To do the polymerization, the substrates were placed in an airtight flask attached to a manifold, which was then evacuated and backfilled with N_2 . This procedure was repeated three times. A solution of octyltrichlorosilane (OTS) in dry n-hexane was prepared in an addition funnel and backfilled with N_2 . The OTS solution was introduced to the substrate dropwise over a period of

15 min and then stirred under N_2 for additional 20 min. The reaction was instantaneous. Siloxanes formed spontaneously by the exposure of OTS to an organic acid under dry conditions according to the synthetic scheme in Figure 3. The samples were then removed from the flask, rinsed in dry n-hexane, and allowed to air dry. They were characterized by PM-FTIRRAS and contact angle measurements.

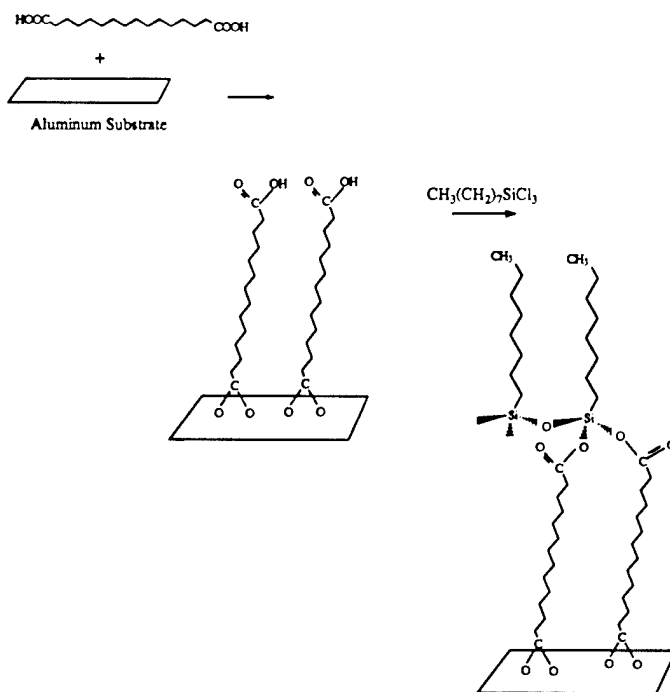


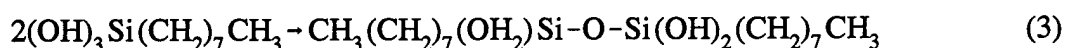
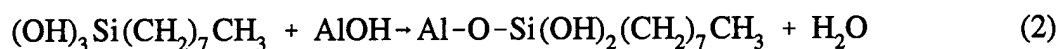
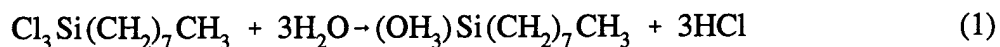
Figure 3. Scheme for Chain Extension and Cross-Linking Acid Terminated SAMs.

Perfluorinated carboxylic acid SAMs were prepared in the same manner as previously described for the HDDA.

3. Results and Discussion

3.1 PM-FTIRRAS Characterization. Self-assembled monolayer samples of HDDA were removed from the solution and rinsed in hexane. Characterization by PM-FTIRRAS showed peaks at $2,854\text{ cm}^{-1}$ (CH_2 symmetric stretch) and $2,920\text{ cm}^{-1}$ (CH_2 asymmetric stretch). No CH_3 stretch in the area of $2,965\text{ cm}^{-1}$ was observed. These results are consistent with known literature values

(Allara and Nuzzo 1985). Cross-linking and chain extension of the terminally exposed acid group is attempted with OTS, according to equations (1)–(3) and the scheme in Figure 3. Notice that this procedure, if successful, has the dual benefit of binding to the acid tail group of the monolayer molecule and cross-linking to other tail groups and itself.



For these samples, the Si-O siloxane bond appears as a broad band at $1,110 \text{ cm}^{-1}$. Because of the overlap associated with the CH_2 stretching modes of the base SAM and the CH_2 stretching of the siloxane overlayer, the reaction of the siloxane could not be confirmed from the spectra in the methylene stretching region between $2,950$ and $2,850 \text{ cm}^{-1}$. To determine whether the siloxane chemistry was occurring at the SAM surface and not the surface of the substrate, a monolayer of pentadecafluoro-octanoic acid (PDFA) $\text{CF}_3(\text{CF}_2)_6\text{COOH}$ was prepared at an aluminum surface. The surface was characterized by PM-FTIRRAS and showed no bands between $2,700 \text{ cm}^{-1}$ and $3,100 \text{ cm}^{-1}$ (see Figure 4a). The signals associated with this film are found between $1,000 \text{ cm}^{-1}$ and $1,500 \text{ cm}^{-1}$ (Tournilhac et al. 1994) and represent CF stretching frequencies (see Figure 4). Following exposure for 15 min to the $\text{SiCl}_3(\text{CH}_2)_7\text{CH}_3$, followed by a complete rinse in hexane, the IR spectra of the substrate changes.

Note the emergence of a response at $2,854 \text{ cm}^{-1}$ and $2,920 \text{ cm}^{-1}$ and a new peak at $2,965 \text{ cm}^{-1}$ that represents a CH_3 asymmetric stretch mode not found on the HDDA. While the siloxane band appears at $1,110 \text{ cm}^{-1}$, all of the CF stretching modes are removed.

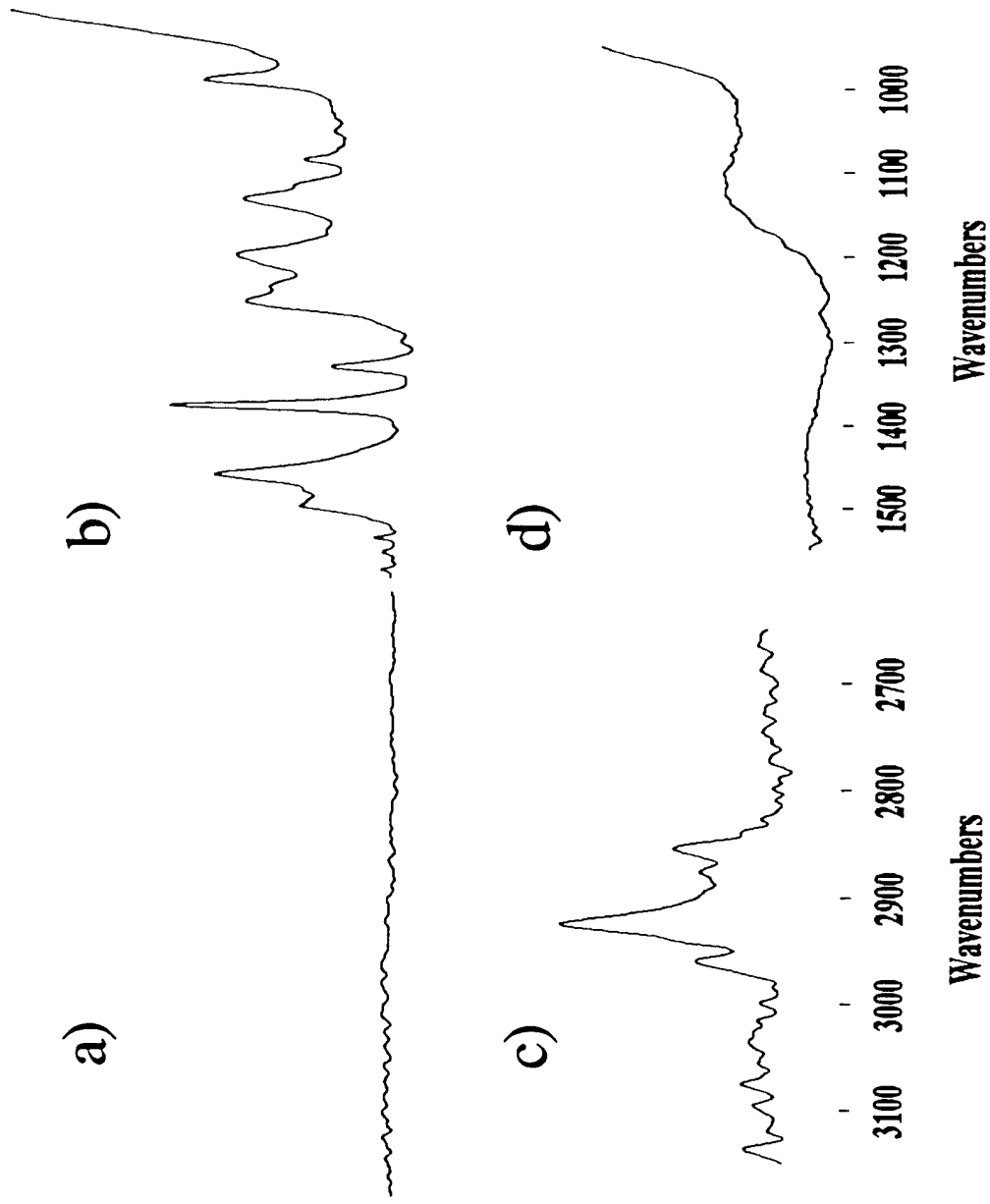


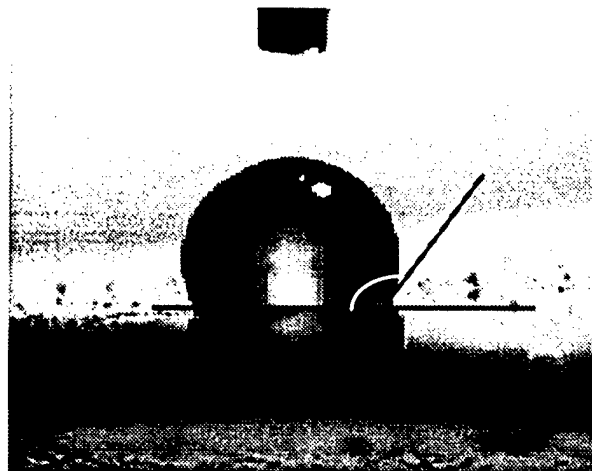
Figure 4. Perfluorinated Monolayer Film (CF₃(CF₂)₆ COOH) Before (a and b) and After (c and d) Silanization.

3.2 Contact Angle Measurements. To confirm the removal of the base HDDA SAM film, contact angle measurements were taken. Single drops of triple distilled water were used as the liquid probe on samples of blank aluminum substrates, HDDA monolayers, and PDFA. The siloxane-treated samples of all of the aforementioned SAM films were also investigated, and the results are compiled in Table 1. As expected, the samples with hydrophilic surfaces such as the HDDA and blank aluminum show low contact angle measurements (83° to 86°) and high wettability. Treatment of any of the samples with OTS increases their measured contact angle to between 108° and 115° (see Figure 5). For samples that have nonreactive head groups such as $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ and $\text{CF}_3(\text{CF}_2)_6\text{COOH}$, exposure to OTS results in an increase in measured contact angle from 98° to 108° and 97° to 109° , respectively. This represents the same approximate contact angle as measured for blank aluminum exposed to OTS (see Table 1).

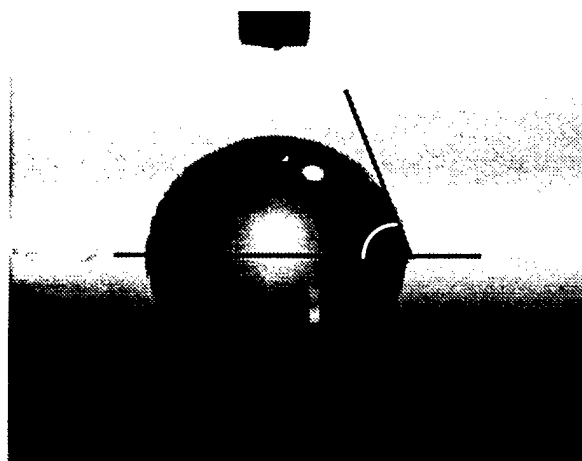
Table 1. Contact Angle Measurements of Monolayer Films on Aluminum

SAM Film	Contact Angle ($^\circ\theta$)
Blank Aluminum	86
Silanized Blank Aluminum	115
$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	98
Silanized $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	108
$\text{COOH}(\text{CH}_2)_{14}\text{COOH}$	83
Silanized $\text{COOH}(\text{CH}_2)_{14}\text{COOH}$	112
$\text{CF}_3(\text{CF}_2)_6\text{COOH}$	97
Silanized $\text{CF}_3(\text{CF}_2)_6\text{COOH}$	109

Due to the combined evidence of the PM-FTIRRAS and the contact angle measurements, we conclude that the silanes preferentially bind to the aluminum oxide surface and thereby remove the SAM, rather than react at its terminal position.



(a)



(b)

Figure 5. Contact Angle of Distilled Water on Blank (a) and Silanized (b) Aluminum Substrates. Angle Bars Added for Clarity.

4. Conclusion

We have prepared SAMs of hexadecanoic acid, HDDA acid, and PDFA. An attempt to extend the chain and cross-link the carboxylic acid tail groups of the HDDA SAM with OTS, resulted in the removal of the base monolayer and replacement with OTS.

The silane has superior antiwetting advantages compared to the organic acid monolayers as shown by its higher contact angle.

Current work involves the use of less-aggressive silane compounds such as amino-propyltriethoxysilane to build the multilayer, or use of trichlorosilanes as the base materials, followed by organic acid multilayer formation.

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6. AUTHOR(S) Lawrence D. Seger, Jeffrey P. Rasimas, Rose Pesce-Rodriguez, and Robert Fifer			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: AMSRL-WM-PC Aberdeen Proving Ground, MD 21005-5066		8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-1553	
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13. ABSTRACT (Maximum 200 words) A self-assembled monolayer (SAM) of hexadecanedioic acid (HDDA) was prepared on an aluminum substrate for purposes of preventing or retarding the consequences of atmospheric corrosion. To enhance the protective qualities of the film, a scheme was developed to polymerize the exposed carboxylic acid functional groups, while enhancing the thickness of the film. To accomplish this, an attempt was made to cross-link the HDDA with octyltrichlorosilane (OTS). Subsequent experiments using a perfluorinated carboxylic acid as the base layer suggest that the OTS is aggressive enough toward the aluminum surface to completely remove the underlying organic SAM and displace it with siloxane (Si-O) linkages at the metal surface. Polarization modulated Fourier transform infrared absorption spectroscopy (PM-FTIRRAS) and contact angle measurements confirm the displacement.			
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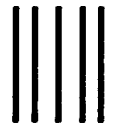
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