Published in final edited form as:

Scanning. 2010 ; 32(5): 304–311. doi:10.1002/sca.20192.

Thermally Driven Stability of Octadecylphosphonic Acid Thin Films Grown on SS316L

Min Soo Lim^{a,*}, Katelyn J. Smiley^a, and Ellen S. Gawalt^b

^a Department of Chemistry, Slippery Rock University, Slippery Rock, PA 16057 USA

^b Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282 USA

Abstract

Stainless steel 316L is widely used as a biomedical implant material; however, there is concern about the corrosion of metallic implants in the physiological environment. The corrosion process can cause mechanical failure due to resulting cracks and cavities in the implant. Alkyl phosphonic acid forms a thin film by self-assembly on the stainless steel surface and this report conclusively shows that thermal treatment of the octadecylphosphonic acid (ODPA) film greatly enhances the stability of the ODPA molecules on the substrate surface. AFM images taken from the modified substrates revealed that thermally treated films remain intact after methanol, THF and water flushes while untreated films suffer substantial loss. Water contact angles also show that the hydrophobicity of thermally treated films does not diminish after being incubated in a dynamic flow of water for a three hour period while the untreated film becomes increasingly hydrophilic due to loss of ODPA. IR spectra taken of both treated and untreated films after water and THF flushes show that the remaining film retains its initial crystallinity. A model is suggested to explain the stability of ODPA film enhanced by thermal treatment. An ODPA molecule is physisorbed to the surface weakly by hydrogen bonding. Heating drives away water molecules leading to the formation of strong monodentate or mixed mono/bi-dentate bonds of ODPA molecule to the surface.

Keywords

Octadecylphosphonic acid; Stainless steel (SS316L); biomaterials; self-assembly; stability; contact angles; atomic force microscopy (AFM); IR spectroscopy

1. Introduction

Biomaterials are defined as synthetic materials that are used to replace or restore function to body tissues and are continuously or intermittently in contact with body fluids (Agrawal, 1998; Davis, 2003). They can be metals or metal alloys (titanium, stainless steel 316 L, and Co-Cr alloys), ceramics (alumina, zirconia, and carbon), or polymers (polyethylene and polyurethane). The range of their applications is large and wide including orthopedics, cardiovascular applications, ophthalmics, and dental applications (Davis, 2003).

Stainless steel 316L (SS316L) has been extensively used for surgical implant materials such as cranial plates, orthopedic fracture plates, dental implants, spinal rods, and joint replacement prostheses due to its lower cost, ease of fabrication, ductility, and viable biocompatibility (Hansen, 2008; Mudali et al., 2003). However, concern about the continued

*Corresponding author: Prof. Min Soo Lim, min.lim@sru.edu, Address: Slippery Rock University, Department of Chemistry, 263 Advanced Technology and Science Hall, Slippery Rock, PA 16057, Tel: +1-724-738-4346, Fax: +1-724-738-4107.

usage of it has been brought up because the corrosion of stainless steel in the body can cause mechanical failure of the implants due to the cracks and cavities initiated by the corrosion process (Hansen, 2008; Mudali et al., 2003; Taira and Lautenschlager, 1992). Furthermore, electrochemical corrosion of the stainless steel implants in the physiological environment releases iron, nickel, and chromium ions which can act as allergens and carcinogens (Hansen, 2008; Mudali et al., 2003). Therefore the surface properties of SS316L determine its success and failure as a biomaterial and thus the surface needs to be treated properly for better corrosion resistance and enhanced biocompatibility without losing its physical and mechanical properties. Several attempts have been made to make a thin protective coating on the surface with the self-assembly method (Mahapatro et al., 2006; Raman et al., 2006; Raman and Gawalt, 2007).

Molecular self-assembly is a method of thin film formation that drives amphiphilic organic molecules to be spontaneously adsorbed and organized on a solid inorganic surface. A few good examples are alkanethiols on noble metals such as gold (Kim et al., 1999; Kim et al., 1997; 1998; Lee et al., 2000; Shon and Lee, 2000) and silver (Rieley and Kendall, 1999; Rieley et al., 1999), alkyl carboxylic acids on metal oxides (Allara and Nuzzo, 1985a; b; Lim et al., 2007; Tao, 1993; Taylor and Schwartz, 2003), alkyl phosphonic acids on mica (Doudévski and Schwartz, 2000; Nie et al., 2005), and alkyl silanes on SiO₂ surfaces (Grange and Markham, 1993; Rhe et al., 1993). Typically, an adsorbing molecule consists of a head group that initiates the molecule to anchor to a solid surface, a methylene backbone chain that influences the packing density of a film by its length (Allara and Nuzzo, 1985a; Tao, 1993), and a terminal group that determines the surface properties of the thin film (Kim et al., 1999; Kim et al., 1997; 1998). The subtle balance between substrate-head group interactions (Rieley and Kendall, 1999) and chain length-dependent intermolecular interactions determines the growth kinetics of the film (Allara and Nuzzo, 1985a; b; McDermott et al., 1997; Tao, 1993; Xiao et al., 1996).

Functionalized (Adden et al., 2006; Quinnes and Gawalt, 2008) and *normal* alkyl phosphonic acids (Gao et al., 1996; Gawalt et al., 2001; Raman et al., 2006; Raman and Gawalt, 2007) have been utilized for the formation of thin films on the metal alloy and metal oxide surfaces due to strong interactions between adsorbing molecules and the substrate surfaces. The thin films formed on the surfaces of biomaterials should exhibit stability under the aqueous environment without being lost through desorption since the implants must interact with biological systems for long time periods with minimal failure. However, little has been done to understand the stability of films under aqueous environment. It has been noted, though, that several research groups treated films thermally (100 – 120 C) before using them for further studies (Adden et al., 2006; Danahy et al., 2004; Gao et al., 1996; Gawalt et al., 2001). They suggest that the thermal process may enhance the stability of films but lack physical evidence.

The present study is the first systematic attempt to document the thermally driven stabilization of ocatadecylphosphonic acid (ODPA) films self-organized on the surface of stainless steel. In this study, ODPA films have been grown on stainless steel 316L surfaces and the enhanced stability of ODPA films after thermal treatment at 100–120C has been tested by flushing modified substrates extensively with methanol, tetrahydrofuran (THF), and water before and after thermal treatment and characterized using atomic force microscopy (AFM), contact angle goniometry, and infrared spectroscopy.

2. Experimental Section

2.1 Materials

Octadecylphosphonic acid (ODPA, 99.0 % purity) was purchased from Alfa Aesar and used without further purification. THF and methanol were purchased from Aldrich Chemical Co. Stainless steel 316L foil (0.5 mm thickness, 99.99% purity, wt%: Fe 66%, Cr 19 %, Ni 10 %, Mn 3 %, and Mo 2 %) was purchased from Goodfellow, Inc.

2.2 Substrate Preparation

SS316L substrates were cut into 1 cm × 1 cm coupons, sanded with 150, 320, 400, and 600 grid sandpapers, and then polished with 400, 800, 1200 grit silicon carbide papers, and 1 μm diamond suspension using Buehler Ecomet 4 mechanical polisher. The polished substrates were flushed extensively with acetone and methanol, cleaned by ultrasonication in acetone and methanol, and immersed in boiling methanol for 10 minutes to remove traces of impurities. The cleaned substrates were stored in an oven at 100 °C for 30 – 60 minutes.

2.3 Film Formation

ODPA thin films were grown on the SS316L substrates as follows: clean substrates were taken from the oven and cooled to room temperature. They were then incubated in 1 mM ODPA in dry THF for 3 – 10 minutes. The first group of samples was thermally treated in an oven at 100–120°C for 30 – 60 minutes and then cooled to room temperature. They were flushed in THF to remove any physisorbed ODPA. A second group of samples was dried in air without thermal treatment, and lightly rinsed in THF. Each sample from both groups was then flushed extensively and independently with methanol, THF, and deionized water, and air dried. For clarification, “samples being flushed with THF” means leaving the samples in a rapid stream of THF and “samples being lightly rinsed with THF” means “dipping samples in THF and slowly removing them” to remove lightly bound material.

2.4 Characterization of monolayers

Atomic Force Microscopy (AFM; Pico SPM, Molecular Imaging)—An AFM was used to analyze the change of surface coverage of the samples before and after they were flushed with methanol, THF, and deionized water. Topographic images of the surfaces were acquired in *non*-contact mode at ambient condition using silicon tips (Veeco Metrology, LLC) with a resonance frequency of 182 – 195 kHz and a force constant of 42 – 48 N/m.

Contact Angle Goniometry—Static contact angles were obtained using a FTA 100 instrument and software from First Ten Angstroms Inc. (Portsmouth, VA) to analyze the wettability of SAMs on the surface. Deionized water droplets of 2 – 5 μl (NANOpure Infinity System, Barnstead/Thermolyne Co.) were placed on the surface in the ambient environment. Measurements were performed within a day of sample preparation and at least 8 replicates were performed.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT; Thermo Nicolet-NEXUS 470 FT-IR)—DRIFT was used to analyze the alkyl chain ordering of the ODPA molecules on the SS316L substrates. The spectra of each sample were collected under a nitrogen environment to eliminate any background signal due to CO₂ and H₂O absorption bands. Cleaned, but unmodified, SS316L substrates were used for background spectra. One thousand twenty four scans were collected of each sample.

3. Results and Discussion

Following adsorption of ODPa to SS316L one group of samples were thermally treated in an oven at 100 – 120°C for 30 – 60 minutes. They were then flushed with THF. A second group of samples were rinsed lightly with THF to remove multilayers and dried in air without thermal treatment. Samples of both groups were then flushed independently with either methanol, THF, or deionized water.

This study employed atomic force microscopy and contact angle goniometry for the first time to investigate the influence of thermal treatment on ODPa film self-organization and stability on the SS316L surface. Figure 1(a) is an AFM image of a thermally treated ODPa film that was taken after it was flushed extensively with methanol. It shows that ODPa molecules adsorb on the SS316L surface and form islands of irregular shapes and sizes. It is posited that the shapes and sizes are dependent on those of irregular topographic features of underlying substrate. Several polish marks that were left in the course of polishing process are seen in the image. Another AFM image in Figure 1(b) was taken from an ODPa film with no thermal treatment after the film was also flushed extensively with methanol. A significant portion of the film was lost during the methanol flush, revealing the underlying substrate surface. It appears from these two images that thermal treatment enhances the interaction between the ODPa molecules and the SS316L substrate and that attached molecules are resistant to methanol flushing. The thermally driven stability of the film was also observed for the ODPa films flushed with THF and deionized water as shown in Figure 1(c) and (d) and Figure 1(e) and (f), respectively. It should be noted, however, that a great portion of film remains on the surface when it was flushed with water as seen in Figure 1(f) even without thermal treatment. This indicates that water flushing is not as effective as methanol and THF flushes in removing a film that is not treated thermally (Figure 1(b) and (d) versus (f)). A 500 nm × 500 nm region (a dotted box) was taken arbitrarily in each image and expanded as shown in an inset. A cross-sectional profile that was taken from the dotted white cross-sectional line from each inset image reveals that each film is likely to be a multilayer. While these thin films are not monolayers as in other reports, the AFM images still show that self-assembled films are much more stable when processed thermally.

Surface wettability estimated from water contact angles can be employed as a measure of surface coverage of hydrophobic and hydrophilic films (Demirel et al., 2007). The influence of thermal treatment on the stability of ODPa films in an aqueous environment was also investigated with contact angle goniometry. Control and modified substrates were immersed in a dynamic flow of deionized water. Each sample was taken from the water at 0, 3, 30, 60, 120, and 180 minutes for contact angle measurements. The contact angle of water on the control substrates (cleaned and diamond polished SS316L which was kept in the oven at 100°C) was 0°. As shown in Figure 2, contact angles were measured from film surfaces and plotted as a function of immersion time in water. Before immersion in water, both samples exhibit comparable magnitude of contact angles of approximately 97° due to the hydrophobic nature of both films. As immersion time increases, the contact angle of the thermally treated film was initially reduced by 5 – 7° and remained in the range of 90 – 92° after 60 minutes. The contact angles of the non-thermally treated samples were reduced by 20 – 22° and maintained in the range of 75 – 78° after a 60 minute immersion. The thermally treated film preserved hydrophobicity while the untreated one lost a substantial degree of hydrophobicity. The results show that the thermally treated films do not expose the surface while the untreated films do. These results confirm the AFM data that showed the enhancement of stability of ODPa monolayer by thermal treatment.

Infrared spectra (Figure 3) of the C H stretching region of the ODPa film on SS316L (a) after thermal treatment followed by a THF flush to remove physical layer, (b) after a THF

flush without thermal treatment, and (c) after a water flush without thermal treatment, respectively are significantly different. Peak positions for the methylene symmetric and asymmetric stretching modes are indicative of the order of methylene backbone chains in the substrate surface (Gao et al., 1996; Gawalt et al., 2001; Raman et al., 2006; Raman and Gawalt, 2007). Aliphatic monolayers characterized by $\nu_{\text{CH2asym}} < 2918 \text{ cm}^{-1}$, and $\nu_{\text{CH2sym}} < 2850 \text{ cm}^{-1}$ are considered to be ordered with all-trans chain configuration. Therefore, peaks in the spectra corresponding $\nu_{\text{CH2asym}} = 2915 \text{ cm}^{-1}$, and $\nu_{\text{CH2sym}} = 2849 \text{ cm}^{-1}$ indicate that remaining residues of the monolayer after THF and water flushes as well as the monolayer thermally treated remain ordered on the surface.

Infrared spectra (Figure 4) of the P O stretching region of (a) ODPa films on SS316L without thermal treatment, (b) with thermal treatment and (c) solid ODPa, respectively indicate surface bonding. All three spectra exhibit bands at 1230, 1232, and 1255 cm^{-1} which are indicative of the presence of P=O bond. Peaks at 900 – 950 cm^{-1} are assigned for P O H stretches. The conservation of this peak at 934 cm^{-1} in spectrum 4a signifies that ODPa molecules are physisorbed on the SS316L surface through hydrogen bonding when the films are not thermally treated. Since multilayers are present on these surfaces, even after thermal treatment with flushing, it is not surprising to see the P-O-H peak persist in some form. Peaks in the 1000–1150 cm^{-1} range can be assigned to P-O stretches. Therefore, in 4a and 4c, it can be seen that there are at least two peaks corresponding to group P-O stretches. This data indicates that there is little change in the head group between the solid state and the deposition onto the surface without thermal treatment. However, in spectrum 4b, only one, broad peak centered at 1078 cm^{-1} is seen. This dramatic change is indicative of a chemical change in the phosphonic acid head group indicating chemisorption to the surface. This emphasizes that ODPa molecules-surface interactions are substantially enhanced after the thermal treatment.

It has been reported previously that bonding alkanephosphonic acid to a metal oxide surface is facilitated simply by heating the films (Danahy et al., 2004; Gawalt et al., 2001). Using DRIFT it has been demonstrated that the ODPa film strongly bound to the surface of native oxide of titanium resists solvent rinsing and mechanical peel testing after thermal treatment at 120 °C for 18 hours (Danahy et al., 2004; Gawalt et al., 2001). In contrast, they found that the same film without thermal treatment was easily removed by solvent rinsing. Their observations agree with what is reported in this study, in that the heating process drives the stability of alkanephosphonic acid on metal and metal oxide surfaces. Raman *et al.* investigated the bonding nature of ODPa SAM on SS316L surface using DRIFT (Raman et al., 2006). The presence of the peaks corresponding to P=O and P O stretching modes and disappearance of the peak corresponding to P O H stretching mode led the authors to a conclusion that ODPa molecules bound covalently to a SS316L surface in a bidentate manner. The data in this study in conjunction with the results of Gawalt (Gawalt et al., 2001), Danahy (Danahy et al., 2004), and Raman (Raman et al., 2006) provides a basis for speculation on the mechanism of stabilizing the ODPa film by a thermal treatment. An ODPa molecule is weakly bound to SS316L surface through physisorption onto a surface-hydroxyl group forming a hydrogen bonding pair (Figure 4). This hydrogen bonding interaction between the ODPa molecules and the surface is weak so that the untreated film can be easily removed by solvent flushes. However, heating the samples drives off water molecules from the surface facilitating the chemisorption of ODPa molecules to the native oxide on the surface. The presence of the peaks for P=O, P O, and P O H as shown in Figure 4(c) leads to the conclusion that an ODPa molecule is chemisorbed on the SS316L surface in a monodentate or mixed mono/bi-dentate manner after thermal treatment, which is strong enough to resist aggressive solvent rinse.

4. Conclusion

The influence of the thermal treatment of ODPa films on SS316L on its stability was investigated in this study. Thermally treated films exhibited substantial stability as measured by resistance to methanol, THF, and water flushes as characterized by AFM. However, non-thermally-treated films lose significant amount of ODPa monomers after flushes with all solvents exposing the underlying substrate. The stability of the film in aqueous environment was investigated with contact angle goniometry. The thermally treated films retained their high hydrophobic character while the untreated samples lost their initial hydrophobicity following immersion in a dynamic flow of deionized water for 0 – 180 minutes. The peak positions corresponding to methylene stretching in DRIFT spectra revealed that the remains of thermally untreated films after water and THF flushes were alkyl-chain ordered like the thermally treated films after the flushes. The presence of the peaks for P=O, P O, and P O H in a DRIFT spectra taken from thermally treated film indicates that ODPa molecules binds to the SS316L surface in a monodentate or mixed mono/bi-dentate manner. A mechanism for thermally stabilizing ODPa film on SS316L has been proposed, that is, ODPa molecules binds covalently to the surface by thermal removal of water molecules from the surface.

Acknowledgments

The authors acknowledge the ACS-Petroleum Research Fund and its donors and National Institutes of Health (NIAMS 1 R15 AR056864-01) for funding of the project. KS thanks NSF-REU/DOD-ASSURE program for a summer fellowship. MSL is supported in part by CHES Research Award (Award number: 200071540) at Slippery Rock University. Professor Aaron Timperman at Department of Chemistry, West Virginia University is acknowledged for the generosity of allowing M. S. Lim to use a contact angle goniometer.

References

- Adden N, Gamble LJ, Castner DG, Hoffmann A, Gross G, Menzel H. Phosphonic Acid Monolayers for Binding of Bioactive Molecules to Titanium Surfaces. *Langmuir*. 2006; 22:8197–8204. [PubMed: 16952262]
- Agrawal CM. Reconstructing the Human Body Using Biomaterials. *Journal of the Minerals, Metals and Materials Society*. 1998; 50:31–35.
- Allara DL, Nuzzo RG. Spontaneously Organized Molecular Assemblies. 1. Formation, Dynamics, and Physical Properties of n -Alkanoic Acids Adsorbed from Solution on an Oxidized Aluminum Surface. *Langmuir*. 1985a; 1:45–52.
- Allara DL, Nuzzo RG. Spontaneously Organized Molecular Assemblies. 2. Quantitative Infrared Spectroscopic Determination of Equilibrium Structures of Solution-Adsorbed n Alkanoic Acids on an Oxidized Aluminum Surface. *Langmuir*. 1985b; 1:52–66.
- Danahy MP, Avaltroni MJ, Midwood KS, Schwarzbauer JE, Schwartz J. Self-assembled Monolayers of α,ω -Diphosphonic Acids on Ti Enable Complete or Spatially Controlled Surface Derivatization. *Langmuir*. 2004; 20:5333–5337. [PubMed: 15986670]
- Davis, JR., editor. *Handbook of Materials for Medical Devices*. Materials Park, Ohio, USA: ASM International; 2003. p. 1-11.
- Demirel G, ağlayan MO, Garipcan B, Duman M, Pişkin E. Formation and Organization of Amino Terminated Self-assembled Layers on Si(001) Surface. *Nanoscale Research Letters*. 2007; 2:350–354.
- Doudevski I, Schwartz DK. Mechanisms of Self-Assembled Monolayer Desorption Determined Using in Situ Atomic Force Microscopy. *Langmuir*. 2000; 16:9381–9384.
- Gao W, Dickinson L, Grozinger C, Morin FG, Reven L. Self-Assembled Monolayers of Alkylphosphonic Acids on Metal Oxides. *Langmuir*. 1996; 12:6429–6435.
- Gawalt ES, Avaltroni MJ, Koch N, Schwartz J. Self-Assembly and Bonding of Alkanephosphonic Acids on the Native Oxide Surface of Titanium. *Langmuir*. 2001; 17:5736–5738.

- Grange JDL, Markham JL. Effects of Surface Hydration on the Deposition of Silane Monolayers on Silica. *Langmuir*. 1993; 9:1749–1763.
- Hansen DC. Metal Corrosion in the Human Body: The Ultimate Bio-Corrosion Scenario. *The Electrochemical Society Interface*. 2008; 17:31–34.
- Kim HI, Graupe M, Oloba O, Koini T, Imaduddin S, Lee TR, Perry SS. Molecularly Specific Studies of the Frictional Properties of Monolayer Films: A Systematic Comparison of CF₃-, (CH₃)₂CH-, and CH₃-Terminated Films. *Langmuir*. 1999; 15:3179–3185.
- Kim HI, Koini T, Lee TR, Perry SS. Systematic Studies of the Frictional Properties of Fluorinated Monolayers with Atomic Force Microscopy: Comparison of CF₃- and CH₃-Terminated Films. *Langmuir*. 1997; 13:7192–7196.
- Kim HI, Koini T, Lee TR, Perry SS. Molecular contribution to the frictional properties of fluorinated self-assembled monolayers. *Tribology Letters*. 1998; 4:137–140.
- Lee S, Shon YS, Ramon Colorado J, Guenard RL, Lee TR, Perry SS. The Influence of Packing Densities and Surface Order on the Frictional Properties of Alkanethiol Self-Assembled Monolayers (SAMs) on Gold: A Comparison of SAMs Derived from Normal and Spiroalkanedithiols. *Langmuir*. 2000; 16:2220–2224.
- Lim MS, Feng K, Chen X, Wu N, Raman A, Nightingale J, Gawalt ES, Korakakis D, Hornak LA, Timperman AT. Adsorption and Desorption of Stearic Acid Self-Assembled Monolayers on Aluminum Oxide. *Langmuir*. 2007; 23:2444–2452. [PubMed: 17261036]
- Mahapatro A, Johnson DM, Patel DN, Feldman MD, Ayon AA, Agrawal CM. Surface Modification of Functional Self-Assembled Monolayers on 316L Stainless Steel via Lipase Catalysis. *Langmuir*. 2006; 22:901–905. [PubMed: 16430246]
- Mcdermott MT, Green JBD, Porter MD. Scanning Force Microscopic Exploration of the Lubrication Capabilities of n-Alkanethiolate Monolayers Chemisorbed at Gold: Structural Basis of Microscopic Friction and Wear. *Langmuir*. 1997; 13:2504–2510.
- Mudali UK, Sridhar TM, Raj B. Corrosion of bio implants. *Sadhana*. 2003; 28:601–637.
- Nie HY, Miller DJ, Francis JT, Walzak MJ, McIntyre NS. Robust Self-Assembled Octadecylphosphonic Acid Monolayers on a Mica Substrate. *Langmuir*. 2005; 21:2773–2778. [PubMed: 15779948]
- Quinones R, Gawalt ES. Polystyrene Formation on Monolayer-Modified Nitinol Effectively Controls Corrosion. *Langmuir*. 2008; 24:10858–10864. [PubMed: 18763818]
- Rühe J, Novotny VJ, Kanazawa KK, Clarke T, Street GB. Structure and Tribological Properties of Ultrathin Alkylsilane Films Chemisorbed to Solid Surfaces. *Langmuir*. 1993; 9:2383–2388.
- Raman A, Dubey M, Gouzman I, Gawalt ES. Formation of Self-Assembled Monolayers of Alkylphosphonic Acid on the Native Oxide Surface of SS316L. *Langmuir*. 2006; 22:6469–6472. [PubMed: 16830984]
- Raman A, Gawalt ES. Self-Assembled Monolayers of Alkanoic Acids on the Native Oxide Surface of SS316L by Solution Deposition. *Langmuir*. 2007; 23:2284–2288. [PubMed: 17266343]
- Rieley H, Kendall GK. X-ray Studies of Self-Assembled Monolayers on Coinage Metals. 3. Angularly Resolved Near Edge X-ray Absorption Fine Structure Determination of the Orientation in 1-Octanethiol SAMs on Ag(111) and Cu(111). *Langmuir*. 1999; 15:8867–8875.
- Rieley H, Kendall GK, Jones RG, Woodruff DP. X-ray Studies of Self-Assembled Monolayers on Coinage Metals. 2. Surface Adsorption Structures in 1-Octanethiol on Cu(111) and Ag(111) and Their Determination by the Normal Incidence X-ray Standing Wave Technique. *Langmuir*. 1999; 15:8856–8866.
- Shon YS, Lee TR. Desorption and Exchange of Self-Assembled Monolayers (SAMs) on Gold Generated from Chelating Alkanedithiols. *J Phys Chem B*. 2000; 104:8192–8200.
- Taira M, Lautenschlager EP. In vitro corrosion fatigue of 316L cold worked stainless steel. *Journal of Biomedical Materials Research*. 1992; 26:1131 – 1139. [PubMed: 1429762]
- Tao YT. Structural Comparison of Self-Assembled Monolayers of n-Alkanoic Acids on the Surfaces of Silver, Copper, and Aluminum. *J Am Chem Soc*. 1993; 115:4350–4358.
- Taylor CE, Schwartz DK. Octadecanoic Acid Self-Assembled Monolayer Growth at Sapphire Surfaces. *Langmuir*. 2003; 19:2665–2672.

Xiao X, Hu J, Charych DH, Salmeron M. Chain Length Dependence of the Frictional Properties of Alkylsilane Molecules Self-Assembled on Mica Studied by Atomic Force Microscopy. *Langmuir*. 1996; 12:235–237.

Figure 1.

AFM images were obtained from thermally treated ODPA films after the films were flushed extensively with (a) methanol, (c) THF, and (e) deionized water. Other AFM images were also obtained from ODPA films without thermal treatment after the films were flushed extensively with (b) methanol, (d) THF, and (f) deionized water. An 500 nm × 500 nm region (a dotted box) in each image was expanded and shown in an inset. A cross-sectional profile was also taken from the dotted white cross-sectional line on each inset image.

Figure 2.

Contact angles were measured from the ODPa films with (filled circles) and without thermal treatment (open circles) and plotted as a function of immersion time in water

Figure 3. DRIFT spectra of the C H stretching region of ODPA film (a) after thermal treatment and THF flush, (b) after a THF flush without thermal treatment, and (c) after a water flush without thermal treatment

Figure 4. DRIFT spectra of the P-O stretching region of (a) ODPA film without thermal treatment, (b) ODPA film with thermal treatment, and (c) solid ODPA.

Figure 5.

A suggested model for the thermally driven stability of ODPA film on the SS316L surface. An ODPA molecule is physisorbed weakly on the surface through hydrogen bonding interaction. Thermal treatment drives away a water molecule, leading to monodentate bonding of the ODPA molecule to the surface.