

Formation and Stability of Alkylphosphonic Acid Self Assembled Monolayers on Electropolished 316L Stainless Steel

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Introduction: Currently available drug-eluting stents (DES) use polymers for coating and releasing drugs. Increasing evidence suggests that inflammatory and hypersensitive reactions are caused by such polymer coatings.¹ Recently, the potential for using self-assembled monolayers (SAMs) as an alternate drug delivery system for coronary stents has been demonstrated.² SAM coatings have been studied on a variety of mechanically polished (MP) metal surfaces. However, commercially available coronary stents are primarily finished by electrochemical polishing (EP). EP stainless steel (SS) has different surface chemistry (increased chromium and hydroxyl group concentrations and decreased iron concentration) than that of MP SS.³ To the best of our knowledge, no reports are available on the formation and stability of SAMs on electropolished engineering metals used for stents such as 316L stainless steel, nitinol, or cobalt-chromium alloy. In this study, we investigated the formation and stability of alkylphosphonic acid SAMs on electrochemically polished 316L stainless steel (SS).

Methods: As-received (mirror polished) 316L SS coupons (1cm × 1cm) were sonicated in acetone followed by electropolishing at a current density of ~0.5 A/cm² in sulfuric acid to phosphoric acid solution (4:6 v/v) with 10% double distilled water (dd-H₂O) maintained at 80±5°C. Mechanically polished (using 1200 grit silicon carbide paper and 1 µm diamond suspension) samples were used as controls. Before SAM deposition, both EP and MP SS specimens were rinsed and sonicated in ddH₂O and methanol for 15 minutes each followed by N₂ gas drying. Thus cleaned SS specimens were immersed in 1 mM dodecylphosphonic acid in tetrahydrofuran for 24 hours. The SAM coated specimens (without rinsing) were annealed in a high temperature furnace at 120 °C for 18 hours under N₂ atmosphere. The stability of SAMs on EP and MP SS surfaces were investigated by immersing the SAM coated specimens in tris-buffered saline (TBS) at 37 °C for 1 hour, sonication in TBS at 37 °C for 1 hour, or sonication in dd-H₂O at 37 °C for 15 min. The specimens were characterized using scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle measurements, and fourier transform infrared spectroscopy (FTIR).

Results/Discussion: SEM images (not shown) of the EP SS surfaces show visible grain boundaries and no directional scratch lines (typical in mechanical polishing) when compared to that of MP surfaces. The average surface roughness values (Ra) of MP and EP specimens were 2.59 ± 0.49 nm and 1.60 ± 0.29 nm, respectively. No significant differences (*p*<0.05) were observed in contact angles for the EP specimens before and after sonication/immersion in TBS at 37 °C for 1 hour or sonication in dd-H₂O at 37 °C for 15 min (Figure 1). However, a significant difference was observed for MP specimens after sonication in dd-H₂O for 15 min. This suggested that the stability of SAMs on EP surfaces might

be better than that of MP surfaces. The FTIR spectra of SAM coated EP and MP SS specimens before and after TBS or dd-H₂O immersion/sonication are shown in Figures 2 and 3. The symmetric and asymmetric stretches of methylene groups are <2850 cm⁻¹ and <2915 cm⁻¹, respectively. This strongly suggests that ordered monolayers were coated on both EP and MP surfaces.⁴ Although the intensity of the peaks reduced after sonication/immersion in dd-H₂O or TBS, the peak positions at ~2848 cm⁻¹ and ~2915 cm⁻¹ indicate that SAM molecules remained ordered on both EP and MP SS surfaces.

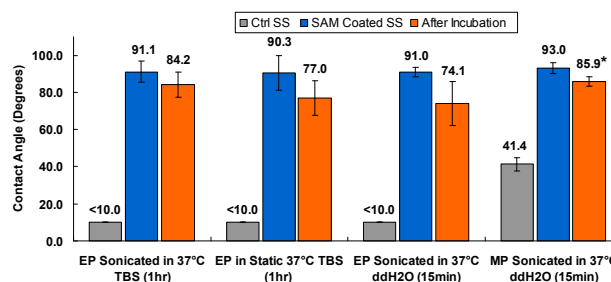


Figure 1. Static water contact angles of SAMs coated EP and MP SS before and after immersion in TBS and ddH₂O. Mean ± standard deviation (n=3). The asterisk (*) indicates statistical significant difference (*p*<0.05) between initial SAM coated SS and after incubation.

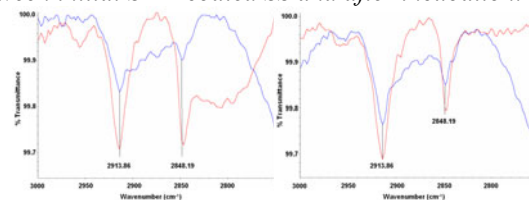


Figure 2. FTIR spectra of EP (left) and MP (right) SAM coated SS before (red) and after (blue) sonication in ddH₂O at 37 °C for 15 minutes.

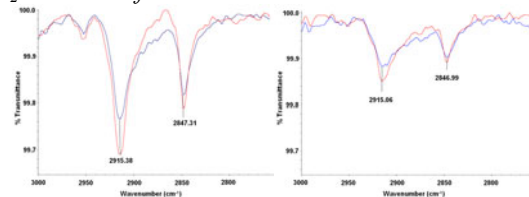


Figure 3. FTIR spectra of SAM coated SS before (red) and after (blue) immersion (left) in TBS at 37 °C for 1 hr and sonication (right) in TBS at 37 °C for 1 hr.

Conclusions: Dodecylphosphonic acid forms a well ordered SAM on EP SS surfaces. SAMs may be more stable in dd-H₂O on EP SS than on MP SS as suggested by contact angle analysis. Although some desorption was observed from both EP and MP surfaces, a majority of the molecules remained ordered and bound to the EP SS surface under physiological conditions.

References: (1) Michael CJ, JACC 2008;1:535-544 (2) Mani G. Biomat. 2008;29:4561-4573. (3) Trigwell, S. Proc.Mat.Proc.Med.Dev.Conf. 2005; 208-213. (4) Raman A. Langmuir 2006;22:6469-6472.