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Retention and Stability of Polystyrene Sulfonic Acid and Polyethylene Glycol Anti- Fouling Films with 3-Aminopropyltriethoxysilane Coupling Agent

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Retention and Stability of Polystyrene Sulfonic Acid and Polyethylene Glycol Anti-Fouling Films with 3-Aminopropyltriethoxysilane Coupling Agent

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Executive Summary

Polymer films have been used in many anti-fouling applications. However, when used in aqueous environments, most hydrophilic low-fouling polymer films are not stable and can be easily disintegrated. Hydrophilic Polystyrene Sulfonic Acid (PSS) and Polyethylene Glycol (PEG) have been used in the past as low fouling materials but have proven to be completely unstable, individually, in aqueous environments. To overcome the problem, PSS and PEG have been thermally cross-linked to improve stability in aqueous environments [2]. The only problem is that when attached to an inorganic substrate, the film retains limited anti-fouling properties and, for most blends, lower stability. A silane coupling agent could be used to increase the stability of the PSS-PEG cross-linked blend films. In earlier studies [3, 14, 15], the addition of APTES as a coupling film on the substrate before adding the polymer, in particular thermoresponsive polymers known as poly(*N*-isopropyl acrylamide) (pNIPAAm) and poly(vinyl methyl ether) (PVME), was employed, and helped increase the stability and retention of the pNIPAAm or PVME polymer to the inorganic substrate, leading to formation of an APTES network around the polymer matrix [3]. This method was used to retain the PSS-PEG films created in the following experiment. Another method previously studied by Dr. Zhang Newby's group at the University of Akron involved chemically grafting APTES onto silicon wafers before spin coating PSS-PEG polymer film onto it [4]. The previous process was attempted in this study; however, was unsuccessful and data could not be used from it.

The goal of this study is to use APTES as a silane coupling agent to increase the stability of PSS-PEG cross-linked polymer film on a hydroxylated substrate and to determine the best option for retaining the polymer film. From the study, it was seen that mixing APTES into PSS-PEG solution, spin coating the mixture followed by thermal annealing at 135° C greatly

increased the retention of the PSS-PEG film. The retention of films was confirmed by water contact angle measurements and dip-washing methods. The films were also visually inspected to evaluate retention.

Generally, the contact angles for APTES treated films were greater than the controls but the p- values proved the averages to not be statistically impactful except for PSS-PEG 75-25 APTES treated films for both Advancing and Receding contact angle measurements. PSS-PEG 55-45 5.0% APTES also showed statistically significant results for Receding contact angle measurements. These results can be seen in **Table 3**. The results show the potential for APTES to retain PSS-PEG polymeric films, but more studies need to be conducted. The addition of APTES in aiding retention can also be seen in photos. In **Table 4**, pictures of before dip-washing and after dip-washing were taken for a sample from each test. For the samples that contained APTES, the films retained quite well. The pictures before and after dip-washing are almost the same, meaning the exposure to water had little to no effect – at least visually – to the retention of the film. Another factor is film thickness. Thickness will increase as more polymer is spin coated onto the film. As seen in **Table 1**, the control samples had thicker films due to having more polymer concentration in them; however, the APTES films had better retention even though they were thinner films. The results illustrated the fact that APTES being mixed with the PSS-PEG creating an entangled matrix led to a better retained PSS-PEG film.

This project helped me improve my research and writing skills while also increasing my knowledge of polymer science. The experimental experience is useful because I am interested in pursuing a career in research and any skills related to this field are invaluable. My hope is that this work can be used to help reduce the pain and suffering in human from biofilm build-up in medical implants while also lowering the cost of the creation of anti-fouling films.

There were some problems with the experiment with the most crucial being that more testing is necessary. It is recommended that the thickness of each film is measured with ellipsometer or by another way. Another recommendation is to use fibronectin, as done by Dr. Zhang Newby's group previously, to assess the anti-fouling properties of each film, not just the retention [2,3]. In general, the addition of APTES to the PSS-PEG polymer film led to greater retention but more studies need to be used.

Introduction

The retention of anti-fouling films is often the most challenging aspect of creating a successful film. The goal of this study is to utilize APTES to retain the already studied PSS-PEG anti-fouling films. The films that are created is a thermally crosslinked network of the polystyrene sulfonic acid (PSS) and polyethylene glycol (PEG) with differing mass fractions (75-25 and 55-45 PSS-PEG). To retain the polymer film, the APTES (3-aminopropyltriethoxysilane) was mixed into the solution, and spin coated into a thin polymer film on a hydroxylated substrate (e.g., silicon wafer), and then thermally annealed in a vacuum oven at 135° C for varying time lengths. This was done to create an APTES network to entrap the polymer film, hence improving the retention of it.

Previous research was conducted in the anti-fouling effects of this material. The research conducted in Dr. Zhang Newby's lab at the University of Akron, which was led by Abdullah Alghunaim, who studied the anti-fouling properties of the retained PSS-PEG films. Abdullah's research focused primarily on the anti-fouling properties of the material and its retention from the curing process of the film with – no added coupling agent. His study was conducted by spin coating PSS-PEG films onto silicon substrates with different mass fractions (i.e., 75-25 PSS-PEG and 55-45 PSS-PEG). The study concluded that retention of the polymer films and their respective anti-fouling capabilities were greatly enhanced by the curing process; the films that were not cured showed almost no retention. However, the retention of the cured films was not robust and to make a better film, the retention of it needed to be further investigated [2]. A project done in the same lab, led by Sean Stybel, conducted a very similar experiment except APTES was grafted onto the surface of the silicon wafer before the film was spin coated on. The research showed a slight improvement in PSS-PEG film retention, but it was not significant [4].

The successful retention of an anti-fouling film can create a plethora of applications. One main application is the longevity of medical implants. Many medical implants must be removed and replaced due to bacterial build up on the implant, which is costly and contributes to human harm. Other applications are in energy storage, water filtration, and food packaging [2]. Anti-fouling films have many different applications and creating a successful film can result in many different applications.

Background

Fouling is a process where particles, proteins, or microorganisms will accumulate onto a material and will cause the material to lose some of its properties [2]. The most common example of this is in the biomedical industry with medical implants. Biofilms, which are films of the bacteria and other microorganisms that will slowly cover a surface in the body, can cause infections in the body and are a growing issue globally. It is estimated that 1-2% of every hip and knee arthroplasties in the U.S.A and UK will result in an infection and the rates are continuing to rise [5]. The infections that rise from these biofilms are hard to treat because they embed themselves deep within the implant and protect the bacteria that is contained within matrix of the film. These biofilms contain mostly polysaccharides, proteins, lipids, extracellular DNA, and bacteria. The biofilms are also integral to the formation of bacteria that are drug resistant [5]. The drug resistant bacteria have been found to be both Gram-positive and Gram-negative [6]. These drug resistant bacteria can be up to a thousand times more resistant to antimicrobial stress than to bacteria of the same species that did not grow in the biofilm. Since biofilms on implants contribute to infections of drug resistant bacteria, the study and creation of anti-fouling polymeric films that can be stable in aqueous environments is essential.

In the design of an anti-fouling polymeric film, the chemicals used in its creation are often picked based on the specific application in which its intended to be used. For biomedical applications, PEG is the most used. The reason PEG is used is due to its film resistance to protein absorption and cell adhesion [8]. Its repulsion to these fouling materials is due to its surface hydration, which is a key parameter of anti-fouling films. It is generally accepted that the interfacial water structure on the polymer surface is critical in determining the efficacy of the anti-fouling film. The stronger the hydration or the stronger the material can bind water molecules to its surface, the better of an anti-fouling property it will exhibit; hence, PEG is a good chemical to create a biomedical bacteria resistant film [9].

To bind the film to a substrate, a coupling agent is needed. Polymeric materials typically do not have strong adhesive forces with inorganic substrates, so a coupling agent is needed. For silica or silicon wafers, the surface needs to be functionalized for the organic polymer to have strong enough interactions to make a stabilized film [10]. Siloxanes are used in many different applications from using poly (siloxane imide) to bind polymers to silica in batteries to binding polymer coatings to piping for corrosion prevention. APTES is a unique coupling agent that can be used in binding polymers to inorganic substrates. APTES can form a network around the polymer and once thermally crosslinked, will lock the polymer in place [3]. The reason this happens is due to APTES having a short alkyl backbone that exhibits low intermolecular forces of attraction, leading to it being unable to form any sort of monolayer. The APTES will instead create a disordered multilayer loose network that polymer chains can diffuse through. Once thermally annealed, the APTES network will no longer have a loose structure and will rigidly hold anything within [3]. A study conducted by Dr. Zhang Newby at the University of Akron investigated this phenomenon. In the study [3], the APTES layer was placed as a coupling film

on the substrate before adding the polymer, using a different polymer known as pNIPAAm, was employed, and helped increase the stability and retention of the pNIPAAm polymer to the inorganic substrate. This was mostly due to the entrapping of the pNIPAAm and coated to the surface as a layer. Then, during a thermal annealing process, APTES molecules segregated through the blend pNIPAAm/APTES layer towards the polymer/substrate interface and the segregated APTES molecules at close vicinity of each other started to cross-link and form a network while allowing the pNIPAAm chains to migrate. As the thermal annealing process continued, the network tightened and was then firmly entrapping the pNIPAAm chains, satisfying a stable polymer film by the entrapment of the pNIPAAm polymer with an APTES network [3]. APTES can bind polymers to inorganic substrates by wrapping them in an APTES network and binding them to the substrate through the siloxane interactions with inorganic substrates [1,3].

Experimental Methods

To make the solutions of each polymer, both PSS and PEG were dissolved in equal mixtures of water and ethanol. Each was made to contain 2.5wt.% of PSS or PEG in their respective solutions. PEG had a molecular weight 50,000 g/mol and PSS had a molecular weight of 70,000 g/mol. The polymer solutions were then mixed by ratios of 55-45 PSS-PEG and 75-25 PSS-PEG. APTES was prepared separately by dissolving APTES in 200 proof ethanol to make 5wt.% solution. To make further ternary blend solutions (PSS:PEG:APTES) for experimentation, APTES was mixed into different solutions of the 55-45 and 75-25 PSS-PEG ratio liquids. APTES was made into two separate concentrations – 5wt.% and 2.5wt.%. This was then mixed turbulently by vortexing into the two different ratios of PSS-PEG. This made 4 separate solutions containing different concentrations of APTES, PSS, and PEG. The solutions prepared were spin-

coated onto silicon wafers to be tested. To prepare the wafers, small pieces of silicon wafer were cut from a large silicon wafer and cleaned using a piranha solution (70:30 H_2SO_4 and H_2O_2 by weight) for 1 hour at about 100°C . After rinsing them with a copious amount of deionized water, wafers were dried with an air stream and placed into UV/Ozone cleaner for 8-10 minutes to be oxidized.

To prepare the polymer film onto the substrate, each solution was spin coated onto the wafers. Spin coater spun about 2000rpm for 1 minutes and then the coated were placed into a vacuum oven to be thermally annealed. The oven was set at 135°C and samples were annealed for 1 week to completely remove all solvent and annealing process. Controls were made of PSS-PEG alone without APTES in the mixture using the same process.

To determine the retention of the films, contact angle and dip-washing of each of film using water were conducted. Water contact angle measurements on the annealed sample were carried out by taking of sessile drops formed on each sample using the goniometer with a CCD camera. The pictures were analyzed with ImageJ software and the contact angles were measured. Along with contact angle measurements, overall retention of the film was assessed by dip-washing the annealed coated wafers into deionized water and optically assessing if each film was retained by visualization and optical pictures.

For each type of films, at least three samples (triplet) were examined to determine the reproducibility and any statistical difference between the types of films. The statistical analysis of the contact angle values was taking the average from each of the trials. Then, the standard average was taken from each trial and both were combined to represent the overall angles produced. From this data, a simple T-test analysis was conducted. The T-test was a two-tailed heteroscedastic test with an assumed confidence interval of 95%. Any p-value produced above

0.05 is thought to be statistically insignificant while values being lower than 0.05 are significant. This is the basis to evaluate the data from contact angle measurements and whether or not the data is remarkable.

Data and Results

The concentration of each component involved in preparing the PSS-PEG films is summarized in Table 1. For the 0 wt.% and 2.5 wt.% of APTES samples, the total solid content was kept at 5 wt.% in the solution. For the 2.5 wt.% and 5 wt.% APTES samples, the total polymer content (PSS-PEG) was kept at 2.5 wt.%. While it was not necessary ideal, we feel the choice of these concentrations provides us a suitable way for comparing the effects of additional APTES on the retention of the PSS-PEG films on the substrate.

Table 1 summarizes the concentration of each component involved in preparing the PSS-PEG films.

Sample	PSS Mass Concentration (%)	PEG Mass Concentration (%)	APTES Mass Concentration (%)
PSS-PEG 75-25 2.5% APTES	1.875	0.625	2.5
PSS-PEG 75-25 5.0% APTES	1.875	0.625	5
PSS-PEG 75-25 Control	3.75	1.25	0
PSS-PEG 55-45 2.5% APTES	1.375	1.125	2.5
PSS-PEG 55-45 5.0% APTES	1.375	1.125	5
PSS-PEG 55-45 Control	2.75	2.25	0

The water contact angles on the processed films (after thermal annealing for 1 week) were measured, with some of the images shown in **Table 2**. Generally, the contact angles were higher for films containing APTES than those without APTES (**Table 3**), especially with 5 wt.% of APTES. The water drops on most of the films were able to maintain their shape, except the 75-25 PSS-PEG control films, where the water drops continued to spread out (i.e., the contact

angle decreased with time). As a result, the advancing angle was found to be lower than that of the static angle and the receding angle was small ($\sim 28^\circ$). This was likely due to the films being unstable and continuously dissolving into water as the drop was placed on it. The 75-25 PSS-PEG films being unstable was confirmed by dip-washing one of them in DI water, where the film was disintegrated (**Table 4**, left image of row 2). The retention of the PSS-PEG films containing APTES was clearly verified with dip-washing (**Table 4**), and the 55:45 blend of PSS-PEG films without APTES were also found to be relatively stable and retained on the silicon wafer, agreeing with what was observed in the previous study [2]. The results show the potential for APTES to retain PSS-PEG polymeric films, but more studies might need to be conducted.

Table 2: Some representing images of water contact angles on the post annealed PSS-PEG films.

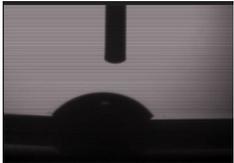
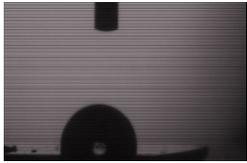
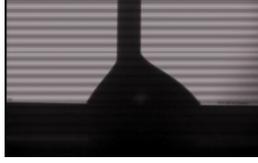
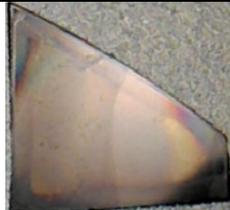
Sample	Contact	Advancing	Receding
PSS-PEG 55-45 Control			
PSS-PEG 55-45 5.0% APTES			

Table 3 shows the resulting contact angle measurements from the study. The contact angles are written as average \pm standard error. The control films compared to the APTES treated films produced higher angle measurements. Each of these measurements were done through pictures and processed by ImageJ, seen in **Table 2**.

Film	Static	Advancing	Receding	p Static	p Advancing	p Receding
PSS-PEG 55-45 Control	61 \pm 8.2	73 \pm 12.6	42 \pm 4.3	--	--	--
PSS-PEG 55-45 2.5% APTES	59 \pm 8.5	77 \pm 4.5	52 \pm 2.0	0.84	0.39	0.13

PSS-PEG 55-45 5.0% APTES	93 ± 8.6	94 ± 6.3	68 ± 3.7	0.06	0.11	0.01
PSS-PEG 75-25 Control	73 ± 6.7	55 ± 1.7	27 ± 2.9	--	--	--
PSS-PEG 75-25 2.5% APTES	79 ± 9.5	107 ± 5.4	77 ± 0.5	0.25	0.001	0.005
PSS-PEG 75-25 5% APTES	83 ± 3.9	95 ± 0.5	62 ± 4.5	0.63	0.01	0.003

Table 4 The appearance of PSS-PEG w. and w/o. APTES after annealing for 1 week at 135° C in a vacuum oven and after a portion of the film being dip-washed in DI water.

Blended PSS-PEG	Control (no APTES)	w. 2.5wt.% APTES	w. 5 wt.% APTES
PSS-PEG 55-45			
PSS-PEG 75-25			

(note: the left portion of the image was dip-washed, the right portion is as the annealed film)

Discussion and Analysis

Retention and stability for each film was assessed by water contact angles formed on the films surface before and after dip washing the films measurements and the visualization (i.e., optical photos) of the film appearances before and after the processed film being dip washed in DI water. Three types contact angles were measured: advancing, receding, and static contact angles. The advancing contact angles were measured by placing the liquid dropper in the drop of water on the surface and increasing the water into the droplet until the three phase contact line advances and the picture of the droplet is taken to measure the contact angle that results. The

receding angle is the opposite; the water from the droplet is withdrawn in the droplet by the water dropper and the three phase contact line recedes, making a new contact angle. The static contact angle is measured by dropping a droplet of water onto to the surface and then measuring the angle that results. Contact angle measurements are used to estimate the surface free energy of the surface. Normally, the larger the contact angle, the lower surface free energy, making a better film [13]. This can be seen in **Table 2**.

As seen in **Table 3**, it is obvious to tell that the APTES increased the retention in the films that contained the 55-45 PSS-PEG mass ratio. The control samples had an average static angle of $61 \pm 8.2^\circ$, advancing angle of $73 \pm 12.6^\circ$, and receding angle of $42 \pm 4.3^\circ$ (**Table 3**). Conversely, the samples with APTES generally had greater contact angles; 2.5% sample had an of $59 \pm 8.5^\circ$ (p-value = 0.84) for static angle, $77 \pm 4.5^\circ$ (p-value = 0.39) for advancing angle, and $52 \pm 2.0^\circ$ (p-value = 0.13) for receding angle while the 5.0% APTES sample had an average of $93 \pm 8.6^\circ$ (p-value = 0.06) for static angle, $94 \pm 6.3^\circ$ (p-value = 0.11) for advancing angle, and $68 \pm 3.7^\circ$ (p-value = 0.01) for receding angle (**Table 3**). As one can see, the more APTES mixed with each sample, the greater the contact angles measured, resulting in a greater retention. For the PSS-PEG 55-45 2.5% APTES sample, the static angle is reported to be lower than the control sample but is statistically insignificant. Most of the sample's T-test in the 55-45 group proved to be statistically insignificant with most p-values being reported as higher than 0.05 which is outside of the 95% confidence interval. Although the APTES treated samples had higher averages, the variance of those samples overlapped with the control sample averages, rendering an inconclusive test. The only sample that had significant results was the PSS-PEG 55-45 5.0% APTES for the receding contact angle, resulting in a p-value of 0.01 (within the 95% confidence interval). The same result can be found for samples

with 75-25 mass fractions of PSS-PEG. The control samples had an average static angle of $73 \pm 6.7^\circ$, advancing angle of $55 \pm 1.7^\circ$, and receding angle of $27 \pm 2.9^\circ$, (**Table 3**). The samples with APTES generally had greater contact angles; 2.5% sample had an average of $83 \pm 3.9^\circ$ (p-value = 0.25) for static angle, $95 \pm 0.5^\circ$ (p-value = 0.001) for advancing angle, and $62 \pm 4.5^\circ$ (p-value = 0.005) for receding angle while the 5.0% APTES sample had an average of $79 \pm 9.5^\circ$ (p-value = 0.63) for contact angle, $107 \pm 5.4^\circ$ (p-value = 0.01) for advancing angle, and $77 \pm 0.5^\circ$ (p-value = 0.003) for receding angle (**Tables 3**). For most measurements, the angle increased as APTES in solution increased as well. As with the 55-45 group, the static contact angles for the 75-25 PSS-PEG films treated with APTES were statistically insignificant despite measuring higher contact angles. For both APTES treated samples – PSS-PEG 75-25 2.5% APTES and PSS-PEG 75-25 5.0% APTES – the advancing and receding angles measurements resulted in p-values that were within the 95% confidence interval. From the angle measurements alone, the increase in APTES did result in higher averages but the p-values did not prove most data to be significant. Since some of the data was significant, APTES has the potential to increase the retention of PSS-PEG films, but more studies are needed to be done to prove this idea.

The role APTES in increasing retention can also be seen in photos. In **Table 4**, pictures of before dip-washing and after dip-washing were taken for a sample from each test. For the controls (no APTES) some non-retained film of the 55-45 blend was removed, but the retained film was mostly intact; whereas the 75-25 blend film began to fall apart from water exposure with parts of the silicon wafer showing through the film, the results agreed to what were observed previously [2]. For the samples that contained APTES, the films retained quite well. The pictures before and after dip-washing are almost the same, meaning the exposure to water

had little to no effect – at least visually – to the retention of the film. Another factor is film thickness. For thickness, the more polymer used, the thicker resulted. As seen in **Table 1**, the control samples had thicker films due to having more polymer concentration in them; however, the APTES films had better retention even though they were thinner films. This illustrates the fact that APTES being mixed with the PSS-PEG creating an entangled matrix led to a better retained PSS-PEG film.

Conclusion

The addition of APTES created a more retained PSS-PEG anti-fouling film. A higher concentration of APTES generally led to greater contact angles and a visually more retained film. The addition of APTES forms a matrix around the polymer and when thermally annealed will lead to an APTES network formed around the polymer that will ultimately bind it to the inorganic substrate. There were some problems with the experiment with the most crucial being that more testing is necessary. It is recommended that the thickness of each film is measured with ellipsometer or by another way. Another recommendation is to use fibronectin, as done by Dr. Zhang Newby's group previously, to assess the anti-fouling properties of each film, not just the retention [2,3]. In general, the addition of APTES to the PSS-PEG polymer film led to greater retention but more studies need to be used.

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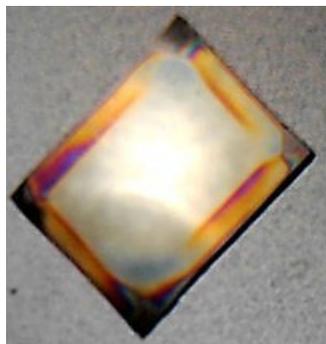
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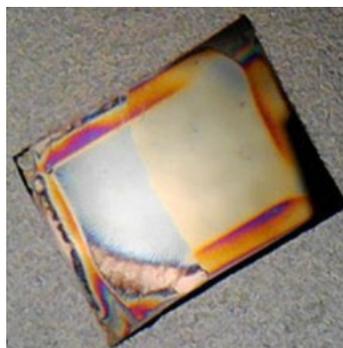
Appendix A

PSS-PEG 55-45 Control

Before dip washing



After dip washing

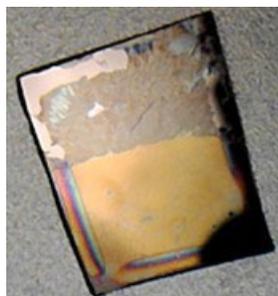


PSS-PEG 75-25 Control

Before dip washing



After dip washing



55-45 2.5% APTES

Before dip washing



After dip washing



75-25 2.5% APTES

Before dip washing

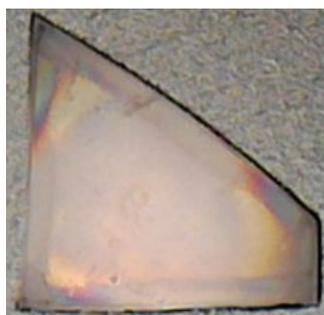


After dip washing



55-45 5% APTES

Before dip washing

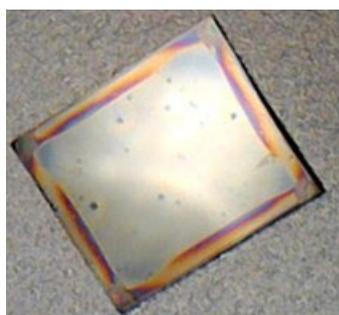


After dip washing



75-25 5% APTES

Before dip washing



After dip washing

