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Stability and Retention Enhancement of Low Fouling Polystyrene sulfonic acid (PSS) and Polyethylene glycol (PEG) Blend Films with Silane Coupling Agents

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**Stability and Retention Enhancement of Low Fouling
Polystyrene sulfonic acid (PSS) and Polyethylene glycol
(PEG) Blend Films with Silane Coupling Agents**

Honor's Project: 4200:497

Sponsor: Dr. Bi-min Zhang Newby

By: Sean Stybel

Executive Summary

The goal of this research project was to prove that the application of silane coupling agents to an inorganic substrate before the addition of a polymer film can help increase film stability and retention, allowing the film to be used in a variety of applications and in aqueous environments where antifouling technology is desired. Previous research had been done where a low fouling film made up of blend of polystyrene sulfonic acid (PSS), a negatively charged polymer, and polyethylene glycol (PEG), a highly hydrophilic polymer was prepared by spin coating a PSS-PEG solution onto a substrate, followed by thermal curing. Although the film proved to have antifouling capabilities, it still lacked reliable stability and retention when tested for water resistance. This research focused on creating crosslinked PSS:PEG films (50:50 and 75:25 by mass fraction) to be retained/immobilized to an inorganic substrate using a coupling silane, 3-Aminopropyltriethoxysilane (APTES). APTES wetted and increased the surface energy of the substrate, leading to more effective bonding. The stable PSS:PEG polymer blend film and similar low fouling films can be applied to medical devices as well as membrane separation processes.

Experimental results showed that the addition of APTES helped increase the film retention percentage from 24-49% for 50:50 PSS:PEG and 22-39% for 75:25 PSS:PEG. Additionally, the contact angles of samples with and without APTES underneath the blend films were consistently hydrophilic at about 15°. Optical microscope analysis showed some non-uniformity and surface spotting, especially with silane treated samples, possibly due to dewetting of the films during the spin coating process. Microscope analysis also revealed similar protein adsorption and less particle attachment associated with the use of the silane coupling agent APTES. It was concluded that the addition of silane coupling agents did lead to increased

stability and retention as well as displayed similar hydrophilicity and increased anti-fouling performance.

This research project helped improve my project planning and managing skills. I was also able to increase my knowledge of polymer technology, theory and testing. This learning will be especially helpful as I pursue a career in the polymer industry and obtain a polymer specialization. Hopefully, my work can be used in order to contribute to the improvement of current technology and become a benefit to society. If successful, this low fouling material can help reduce the surgical removal of medical implants, thus reducing the pain/suffering of patients and healthcare costs; lower the costs of antifouling coatings in many industries such as reducing contamination of microorganism in food packaging or reducing the deposition of dust and other debris on solar panels to achieve a greater solar energy harvesting.

In future research it would be worthwhile to measure the charge of the surfaces, possibly through zeta potential analysis. If a noticeable increase in negative charge is present in the samples containing more PSS, then the 75:25 PSS:PEG substrates would theoretically have better anti-fouling properties. It is also recommended that extra precaution is taken in order to avoid silane contamination. The oven must be properly cleaned and samples containing silane should be separated from other samples. Finally, it is recommended that the humidity is better controlled during spin-coating, especially from ethanol solution, and that dewetting prevention becomes a larger priority in order to produce more uniform coatings. Once these steps are followed, and several consistent and improved results are recorded, the research can proceed to a larger scale.

Introduction

The application of silane coupling agents to an inorganic substrate before the addition of a polymer film can help increase stability and retention of the polymer film, allowing the film to be used in a variety of applications. Specifically, this research was aimed at enhancing the stability and retention of a crosslinked polystyrene sulfonic acid (PSS) and polyethylene glycol (PEG) film (50:50 and 75:25 by mass fraction). Experiments were therefore carried out by chemically grafting silane to the substrate using 5% wt 3-Aminopropyltriethoxysilane (APTES) solution in order to be used as a low-fouling material.

The negative charge of PSS as well as the high hydrophilicity of PEG creates a fouling resistant film [1]. However, based on research done in Dr. Zhang Newby's lab at the University of Akron, the stability of the film and its retention on a substrate without the APTES are limited. Silane coupling agents wet and increase the surface energy of a substrate, leading to more effective bonding [2]. Coupling agents are also used to generate a water resistant interface between a polymer layer and glass substrate. Once stable, the PSS:PEG polymer blend and similar low fouling films can be applied to applications in aqueous environments such as medical devices and membrane separation processes.

By improving the stability and the retention of such low fouling films, which can be generated following a simple two or three step process, the utilization of this technique in industry can lead to low cost production of antifouling surfaces that are important in many fields (e.g., biomedical, maritime industry, food packaging, water and oil purification, and energy harvesting). Successful low fouling material can help reduce the surgical removal of medical implants, thus reducing the pain/suffering of patients and healthcare costs; lower the costs of antifouling coatings in many industries such as reducing contamination of microorganism in food

packaging or reducing the deposition of dust and other debris on solar panels to achieve a greater solar energy harvesting [1].

Background

Fouling occurs when particles, macromolecules (such as proteins), and microorganisms accumulate on a surface and cause a negative impact on the effectiveness of the fouled device. Fouling can cause medical devices in aqueous biological environments to fail and require removal [1]. Fouling is also prevalent in membrane separation processes where it leads to decreased permeability and increased energy consumption [1]. Many organic foulants, including bacteria and proteins, carry a net negative charge in water, which increases the likelihood of a positively charged material fouling compared to a negatively charged material [1]. It is also known that surface hydrophilicity can increase the fouling resistance of many different polymeric materials [1].

Foulants physically react and chemically degrade devices and materials. Membranes, for example, experience a reduction in flux caused by permanent fouling [3]. Fouling can increase membrane electrical resistance, followed by an increase in energy consumption and a shortened membrane life [4]. The combination of surface thrombus and biofilm formation that eventually prevents a medical device from functioning properly is called biofouling [5]. It is currently estimated that humans with medical device implants are at a 65% risk for bacterial related infections associated with the growth of bacterial biofilms on device surfaces [5]. Once biofouling of a medical device results in failure, it can only be corrected by replacement through a costly invasive procedure [5]. Current antifouling products under development must not only be effective but environmentally friendly as well. For example, the EU Biocide Products

Directive created restrictions for the use of leachable biocides on marine coatings, increasing the interest in finding environmentally friendly preventative methods [6].

Although negatively charged grafted surfaces are typically stable, the chemicals used for grafting are sometimes hazardous to the environment [3]. Also, grafting by gamma ray and UV irradiation, or in the plasma chamber, cannot yet be easily replicated and applied on an industrial scale [3]. It is known that poly(N-vinyl-2-pyrrolidone) (PVP), when blended to polysulfone can produce a hydrophilic surface [3]. However, PVP leaching will eventually occur during use [3]. Further research has been done by performing surface modification of an anion exchange membrane with a polyelectrolyte (sodium 4-styrene sulfonate) [4]. Polyelectrolytes contain an electrolyte group that dissociates in aqueous solutions, thus charging the polymers. Results indicated that both hydrophilicity and negative charge density were increased; therefore, the surfaces antifouling potential was improved [4]. In other studies, polyelectrolyte multilayers created with poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrene sulfonate) demonstrated antimicrobial properties without the use of specific biocides for marine applications [6].

Hydrophilic low-fouling surfaces share similar structural and chemical properties including electrical neutrality and the capacity to form hydrogen bonds [5]. Hydrophilic surfaces prevent the adhesion of fouling agents to the material surface by forming a physical barrier called the hydration layer [5]. The hydration layer is created by hydrogen bonding between the functional groups on the device surface and the water molecules present in the environment [5]. The strength of the hydration layer directly effects the effectiveness of hydrophilic materials [5]. Hydration layer strength is determined by the physiochemical properties of the material, such as the molecular weight of the polymer and the conformation of the polymer chains [5]. PEG is

currently the most commonly used material for preparation of low-fouling medical devices because of its resistance to nonspecific protein adsorption and cell adhesion due to the formation of a strong hydration layer with the surrounding environment [5]. Alternative materials to PEG include polyamides, polyurethanes, and naturally occurring polysaccharides, including chitosan and dextran [5].

Recently, Dr. Zhang Newby's research group has tested the antifouling ability of a crosslinked blend of polystyrene sulfonic acid (PSS), a negatively charged polymer, and polyethylene glycol (PEG), a highly hydrophilic polymer. A PSS-PEG film was prepared by spin coating a PSS-PEG solution onto a substrate, followed by thermal curing. The research results proved that there was a slight improvement in resistance to non-specific protein adsorption when compared to sulfonic acid and PEG controls and similar low attachment results compared to PEG controls toward particle and bacterial cells [1]. However, the film stability and retention, measured by ellipsometer thickness and by dip-washing, was not optimal, especially with films containing a larger ratio of PSS. It was then hypothesized that the stability could be improved by the utilization of silane coupling agents, specifically APTES, at the polymer film and inorganic substrate.

Any monomeric silicon chemical is called a silane. If the silane contains at least one silicon-carbon bond it is referred to as an organosilane [7]. Carbon-silicon bonds are known to be very stable and nonpolar [7]. Both low surface energy and hydrophobic effects have been observed when carbon-silicon bonds are in the presence of an alkyl group [7]. Organo-functional silanes are molecules that carry two different reactive groups on their silicon atom so that they can react and couple with an assortment of materials such as inorganic surfaces and organic

resins [7]. The coupling to these materials is usually accomplished by covalent bonding or via a polymeric transition layer between the different materials [7].

The discovery of the application of organo-functional silanes as coupling agents occurred in the 1940s during the research and development of fiberglass-reinforced composites [7]. Researchers soon discovered that although the composites were very strong with high strength and modulus at a reduced weight, a loss of bond strength between the fiber glass and resin occurred rapidly when aged underwater [2,7]. Eventually, researchers found that specific organo-functional silanes actually barred the entrance of water and bond displacements at the fiber/resin interface, therefore limiting delamination, while increasing the initial composite strength [2,7]. The coefficient of thermal expansion for the glass fiber is much lower than that of the polymer resin [2]. If the polymer composite is exposed to extreme temperature cycling, the difference between the thermal expansion coefficients can lead to stresses at the interface between the organic polymer and inorganic substrate [2]. It is possible that the stresses at the interface may exceed the strength of the composite [2]. Consequently, it is imperative that coupling agents guarantee that the physical properties of the reinforced material remain relatively unchanged by moisture and humidity and reduction of stress at the interface during excessive thermal cycling occurs [2]. Other applications for silanes such as the treatment of fillers to enhance reinforcement and additives in inks, coating and sealants in order to bolster adhesion or in plastics and rubbers to aid crosslinking have since been discovered [7].

Most of the popular organosilanes have one organic substituent and three hydrolyzable substituents [8]. Organo-functional silanes are characterized on a molecular level as having two different types of reactive groups, OR and X. The OR groups are hydrolyzable and include methoxy, ethoxy and acetoxy groups [7]. Group X represents an organo-functional group such as

epoxy, amino, methacryloxy, or sulfide [7]. The existence of some Si-alkyl groups helps ensure low surface tension and adequate wetting properties [7]. Si-OR bonds hydrolyze readily with water in order to form silanol Si-OH groups [7]. The silanol groups can then condense with each other in order to create polymeric structures with very stable siloxane Si-O-Si bonds [7]. Then, the silanol groups create hydrogen bonds with metal hydroxyl groups on the surface of glass, minerals or metals and subsequent condensation occurs in order to be able to create stable Si-O-M bonds [4,7]. The covalent linkage is ultimately formed with the substrate during a drying or curing stage and is known as the chemical bonding theory first proposed by Arkles and Plueddemann [2,4]. The very flexible polymeric siloxane backbone allows the interface to adjust to any steric constraints from the oxide filler surface [2]. This capability allows for surface treatment, coupling and assembling of different surfaces chemically such as between organic and inorganic materials [7]. Although described in an orderly fashion, these reactions may occur simultaneously after the initial hydrolysis step [8]. The interface usually only contains one bond from each silicon of the organosilane to the substrate surface [8]. The other two silanol functional groups are either condensed or in free form [8]. The remaining group is available for covalent reaction or physical interaction with different phases [8]. The vast majority of surface treatment applications hydrolyze the alkoxy groups of the trialkoxysilanes in order to form the silanol containing species, which in turn increases the water resistance of the reinforced composite product [2]. They are applied from dilute aqueous solutions, as partial hydrolysates, or from organic solvents (usually alcohols) [2]. Over 60% of the treated glass fiber market uses γ -aminopropyltrialkoxysilane for their products [2]. Since the degree of oligomerization and crosslinking correlates to coupling agent effectiveness, it is recommended that the silane is

supplied very shortly after manufacture so that they are not already partially oligomerized and/or crosslinked prior to use [2].

The water for hydrolysis to take place may be added directly, come from the atmosphere, or already be present on the substrate surface [8]. The degree of polymerization of the silanes is dependent upon the amount of available water and organic substituent [8]. Too much water will result in excessive polymerization in the solvent phase, and too little water will result in the formation of an incomplete monolayer [8]. If the silane that is added to the water has a low solubility, it is more likely that there will be a high degree of polymerization [8]. It is also important to know the acidity of the silane solution, as basic and acidic conditions affect the relative rates of silane hydrolysis and condensation [2]. Additionally, multiple organic substitution will favor the formation of stable monomeric silanols [8]. The thickness of a polysiloxane layer can be determined by the concentration of the siloxane solution [8]. Deposition from a silane solution onto glass usually results in several molecular layers that are interconnected by a loose network structure and/or intermixed [8]. The orientation of functional groups on the surface of the substrate is usually horizontal, although not necessarily planar [8]. Covalent bond formation on the substrate surface is a somewhat reversible process [8]. Bonds may break and reform to relieve internal stress from water removal occurring by heating to 120°C for 30 to 90 minutes or evacuation for 2 to 6 hours [8]. It has been noted that improved composite properties occur when hydrolysis and condensation reactions are in equilibrium and lead to the formation of a silane/siloxane interface at the surface [2]. It should also be noted that the drying conditions used for the silane treated substrate can also affect the structure of the absorbed silane [2]. The temperature and length of the drying period both influence the number of siloxane bonds formed between adjacent silanes as well as with the surface [2].

It is important that the properties of the organo-functional silane match the reactivity of the resin with appropriate groups on the silane in order to effectively react with the resin [7]. It is also important that the organo-functional silane matches the solubility parameter of the adjacent resin to create a smooth transition at the interface [7]. If the oligomeric siloxane layer and the polymer resin are compatible, a copolymer can result when cured [2]. However, if they are only partially compatible, the resin and siloxane will cure separately, creating an interpenetrating polymer network both on the substrate and within the polymer matrix [2]. The creation of an interpenetrating network (IPN) at the boundary interface contributes to improved adhesion found with thermoplastic polymers [7]. Solvent, concentration, reaction time and reaction temperature all have an effect on attachment kinetics [2]. Furthermore, the three main areas that have utilized organo-functional silanes are mineral filler treatment, crosslinking aids, and adhesion promoters [7].

Mineral fillers are currently being used in industry as modifiers for reinforcing organic polymers, thermoplastics and thermosets [7]. However, the hydrophilicity of metal hydroxyl groups on the mineral filler surface are incompatible with organic polymers [7]. Organosilanes can treat the filler surface, increasing its compatibility and ability to disperse in the polymer [7]. Additionally, any minerals that have silicon or aluminum hydroxyl groups on their surface can be treated with organo-functional silanes [7]. The silanes will create better dispersion and improve wetting and adhesion to the polymer [7]. The polymer and filler mix will in turn display a lower mix viscosity and enhanced mechanical properties [7].

One way to improve performance polymers and polymeric composites is to crosslink them to some degree [7]. It has been proven that partially crosslinked polyethylene can be produced by using organo-functional silanes [7]. For crosslinking to occur, vinyl-functional

alkoxy silanes are grafted onto the polyethylene chains by using peroxide as an initiator [7]. The vinyl groups are responsible for grafting on the polyethylene backbone, while the alkoxy groups are responsible for crosslinking between the polyethylene chains when exposed to heat and moisture [7]. This technology is primarily used for pipe, wire and cable insulation [7]. Silanes are also used in crosslinking of thermoplastic vulcanisates, improving mechanical properties [7].

Organo-functional silanes are most commonly known for surface modification. They are used as additives that improve adhesion between two seemingly incompatible materials because of their low surface tension, high surface energy, enhanced surface wetting, reactivity to different surfaces, and their ability to create interactions as well as a sufficient interface between an adhesive layer and substrate for bonding [2,7]. Thus, it is possible for a hydrophobic matrix to adhere to hydrophilic surfaces [2]. Silanes are able to modify surfaces under anhydrous conditions that are consistent with monolayer and vapor phase deposition requirements [2]. The selection of trialkoxysilane coupling agents may, in fact, contribute to poor water resistance properties of the composite because the treated surface will remain hydrophilic [2]. This can be countered by using very dilute silane solutions or by washing the treated surface with the appropriate solvent to remove excess, non-covalently bound silane [2]. It has also been determined that using excessive amounts of silane at the interface can result in reduction of composite fracture toughness due to the high brittleness of the resin product [2].

Today, researchers and engineers are focused on producing silanes and processing conditions with low volatile organic compounds (VOCs) [7]. Typically, Organo-functional silanes rely on the hydrolysis of a Si-OR group and condensation that occurs for coupling with inorganic surfaces and crosslinking plastics [7]. Increased regulation and health concerns have led to the introduction of products with less hydrolysis and condensation byproducts [7].

Prehydrolyzed silanes, water based silane solutions, solid carrier supported silanes to be added during plastic extrusions, and plasma surface treatment along with silanes are all currently under development [7].

The silane tested in this project is 3-Aminopropyltriethoxysilane (APTES), which is widely used as an adhesion promoter and has demonstrated the ability to prevent dewetting of thin polymer films from substrates [9], enhance stability of polymer thin films on substrates [10] and retain polymers on surfaces [11-13]. APTES is also one of the most commonly used organosilane coupling agents on silicon containing substrates [14]. Prior research confirmed that stable APTES films on silicon wafer substrates can be produced with proper curing [9-14]. APTES has an advantage over similar organic compounds as a coupling agent because it can bond to the substrate through several mechanisms due to its active terminal amino group (-NH_2) and the three silanol (-OH) head groups once the APTES molecule is fully hydrolyzed [9,15]. van der Waals forces, hydrogen bonding, and covalent bonding can all happen through both -NH_2 and -OH groups [9, 13, 15]. The silane is therefore capable of competing with water for hydroxylated surfaces [9, 12-13, 15]. With heating, hydrogen bonds can be broken, leading to more silanol groups being available for condensation and formation of siloxane linkages and tightening of the three-dimensional network [9-13]. When a polymer thin film comes into contact with the APTES layer during the heating process, the polymer chains can diffuse into the APTES network while the network is being tightened by the additional crosslinking [9-13]. The penetrated and entrapped chains could help in stabilizing the polymer thin film on the substrate [9-13]. Earlier research in Dr. Zhang Newby's group has confirmed that spin coating APTES in a blend with poly(*N*-isopropylacryl-amide) (pNIPAAm) or simply coating pNIPAAm on an APTES layer grafted to a silicon wafer or glass slide enhanced the retention of pNIPAAm on the

surface after a thermal annealing process [11-13]. The approach will be adopted in this project to enhance retention and stability of PSS-PEG blend thin films on the surface.

Experimental Methods

Polymer solutions were prepared by first dissolving 20,000g/mol PEG in a solvent mixture containing an equal amount by weight of water and ethanol to 2.5wt% PEG. Then, 18% 75,000g/mol PSS in water was diluted with water and ethanol so that there were equal amounts of water and ethanol in solution and 2.5%wt PSS. The polymer solutions were then mixed in either weight ratios of 50:50 PSS:PEG or 75:25 PSS:PEG. APTES solution was prepared separately by diluting APTES with ethanol solvent to 5%wt in solution.

Clean substrates, either glass slides or silicon wafers, were prepared by first cutting them into small squares and then immersing them in piranha solution (70:30 H₂SO₄:H₂O₂ by weight) for 1hr at 100°C. The substrates were then rinsed with deionized water and dried using an air stream. The substrates were then placed in a UV/Ozone cleaner for 8 min where they could be further oxidized.

The polymer film was prepared using a spin coater set to 2000rpm and a 60s cycle time and at about 20% humidity. First, the APTES solution was spin coated onto the substrate and allowed 2hr to dry. Then, the PSS:PEG solution was applied via spin coating. The humidity was adjusted as needed using a heating lamp. The samples were then heated at 40°C for 1hr in order to remove remaining solvent. The coated substrates were then put in a vacuum oven and cured at 135°C for 14hr. Several substrates coated with solely PSS:PEG or APTES were used as controls.

The contact angle of water cured polymer films and controls were measured with a contact angle goniometer with a CCD camera attachment using the sessile drop method. Liquid drops were imaged and contact angles were measured using computer software.

The stability and retention of the cured PSS-PEG film was evaluated by dip-washing coated silicon wafers in water and measuring film thickness using an ellipsometer. Polarizer and analyzer data was gathered in order to be entered into ellipsometry software to determine the thickness of each film before and after dip-washing. Further analysis was carried out by naked eye and optical microscope.

Fluorescent particle attachment experiments were carried out using 7×10^6 particles/mL in 0.1× PBS and 1×PBS at room temperature. The particles were applied to cured and rinsed films and controls and analyzed under fluorescent light and using an optical microscope.

Protein adsorption experiments were carried out using 20µg/mL in 1 × PBS fibronectin and BMS solutions. The protein was applied to cured and rinsed films and controls and adsorption was carried out at 37°C for 1hr. Each sample was placed in a covered water bath in order to prevent liquid evaporation. After 1hr, the samples were again rinsed with water in order to remove non-absorbed fibronectin molecules and residual salt coming from the buffer. The samples were then submerged in water and analyzed under an optical microscope and using fluorescent lighting.

Data and Results

Table 1. The static water contact angle of each cured PSS:PEG sample with and without APTES was measured with four different samples, all coated on silicon wafer substrates. Each recorded measurement is an average out of three. The substrate coated with APTES alone had an average contact angle of 65.02° . The silicon wafer alone had an average contact angle of 7.22° .

	Contact Angle ($^\circ$)			
	50:50 Control S	75:25 Control S	50:50 APTES S	75:25 APTES S
	10.758	9.904	9.856	5.595
	10.931	8.931	14.538	16.065
	19.916	21.801	13.069	8.616
	23.531	24.087	21.038	21.961
Average	16.284	16.181	14.625	13.059

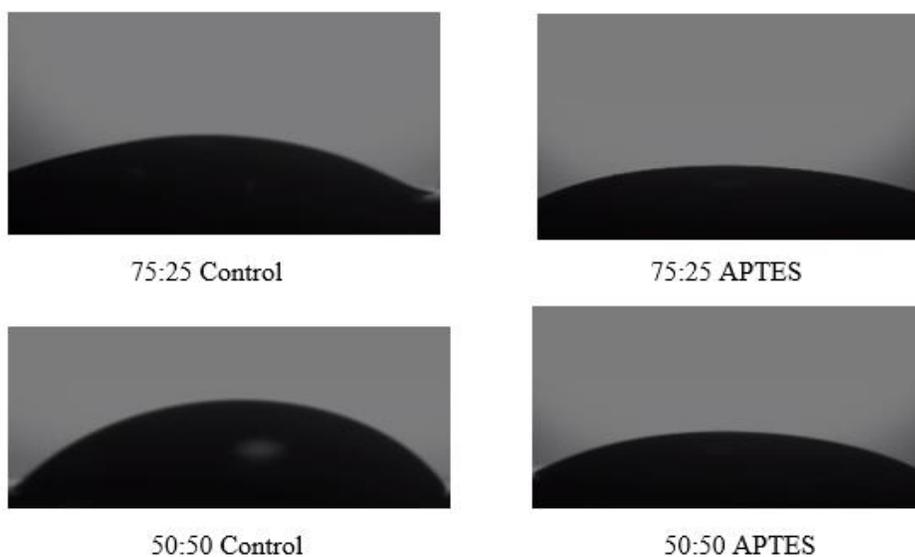


Figure 1. Shows representing photographs of water contact angles on a set (the 4th set from **Table 1**) of samples.

Table 2. Shows the ellipsometer thickness measurements in Å for 6 different sets of cured PSS/PEG blend samples. The average thickness of APTES per sample was determined to be 245 Å and was therefore subtracted from necessary measurements in order to focus on PSS:PEG polymer film thickness. A refractive index of 1.460, average delta and average psi values were used in the calculations.

After Curing						
Sample	Thickness (Å)					
spin-coated	Set 1	Set 2	Set 3	Set 4	Set 5	Set 6
50/50 control	3520	4096	3635	3454	3765	3915
50/50 on APTES	2842	3065	3441	3105	3479	2974
75/25 Control	3923	3851	-	3768	4230	4138
75/25 on APTES	3246	3061	-	2984	3228	3143

Table 3. Shows the ellipsometer thickness measurements in Å for 6 different sets of samples after dip-washing the cured PSS:PEG samples. The average thickness of APTES (245 Å) has been subtracted from necessary measurements in order to focus on PSS:PEG polymer film thickness. A refractive index of 1.460, average delta and average psi values were used in the calculations.

After Dip-Washing						
Sample	Thickness (Å)					
spin-coated	Set 1	Set 2	Set 3	Set 4	Set 5	Set 6
50/50 control	143	1167	1264	1380	1255	249
50/50 on APTES	232	1000	3149	1064	962	2907
75/25 Control	198	358	-	1360	1153	1333
75/25 on APTES	468	271	-	1167	1156	3072

Table 4. Shows the PSS:PEG polymer film retention percentage after dip washing. The retention percentage was calculated by dividing the thickness after dip-washing by the original cured thickness.

Sample	Retention (%)						
spin-coated	Set 1	Set 2	Set 3	Set 4	Set 5	Set 6	AVG
50/50 control	4	28	35	40	33	6	24
50/50 on APTES	8	33	92	34	28	98	49
75/25 Control	5	9	-	36	27	32	22
75/25 on APTES	14	9	-	39	36	98	39

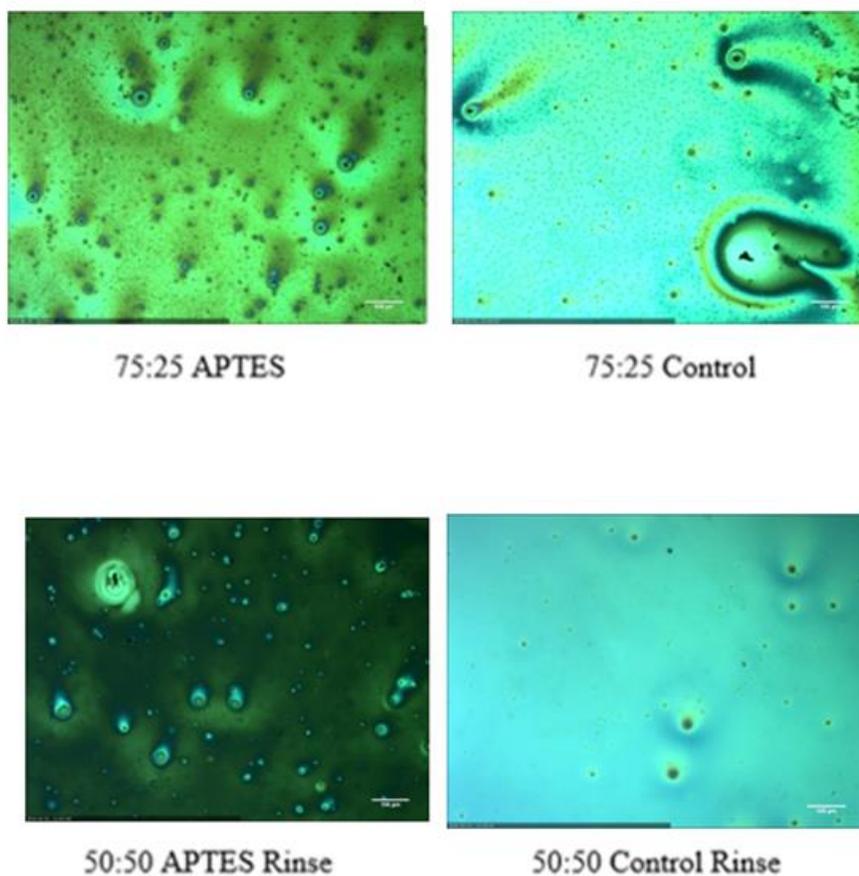


Figure 2. Shows good examples of the differences in surface appearance between cured samples and samples rinsed with deionized water. These photographs were taken during optical microscope analysis. Scale bars (106 μ m) can be found at the bottom right corners of the images.

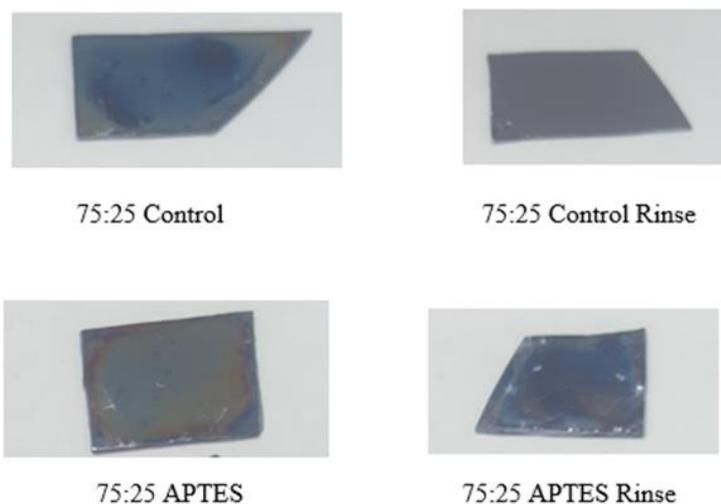


Figure 3. Shows examples of the differences in surface appearance between cured samples and samples rinsed with deionized water. These photographs were with a standard handheld camera and are from set 1 as referenced in **Tables 2-4**.

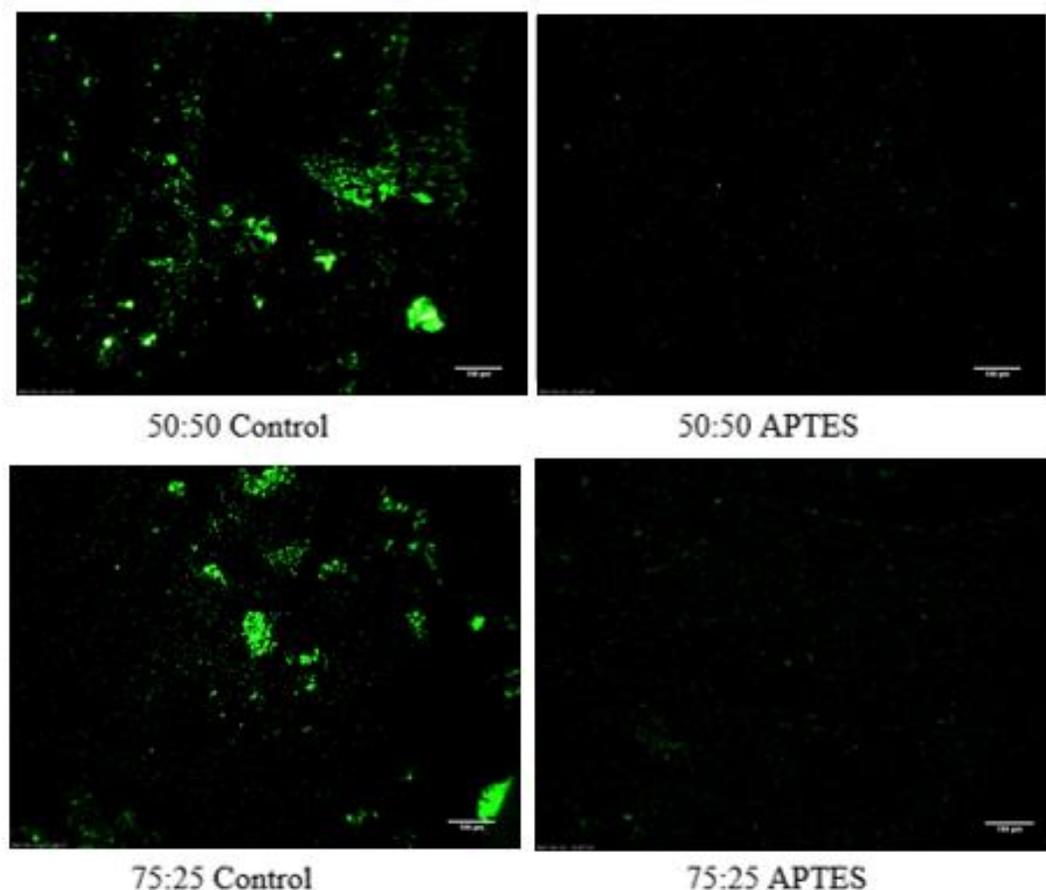


Figure 4. Shows the differences in 7×10^6 particles/mL in $0.1 \times$ PBS attachment concentration between cured samples with and without APTES after rinsing with deionized water using an optical microscope with fluorescent lighting. Scale bars ($106\mu\text{m}$) can be found at the bottom right corners of the images.

Discussion/Analysis

As seen in **Table 1** and **Figure 1**, the contact angles measured for all samples were hydrophilic. There was very little variation between measurements, even though it was theorized that the samples containing a larger portion of PEG would be increasingly hydrophilic. These measurements also showed that the addition of APTES coupling agent had little effect on the hydrophilicity of the above polymer film, even though the APTES is a more hydrophobic substance itself. With these results, it would be worthwhile to measure the charge of the surfaces,

possibly through zeta potential analysis. If a noticeable increase in negative charge is present in the samples containing more PSS, then the 75:25 PSS:PEG substrates would theoretically have better anti-fouling properties.

According to **Table 4**, the polymer films with the addition of silane coupling agents overall performed better than the films cured directly on the substrates. The discrepancy within the data in sets 4 and 5 is believed to have been caused by silane contamination in the vacuum oven during curing. The APTES escaped from its substrates in the vapor phase and contaminated the surface of the oven as well as any other controlled substrates present. This addition of APTES from controls increased the bonding strength of the PSS:PEG to the substrates and led to little variation in retention results for two specific sets. After set 5, the oven was thoroughly cleaned with acetone and the controls were separated from the samples containing APTES during the curing stage. Set 6 yielded much more variation between control and experimental samples, as well as near complete a retention of the original film for APTES coated substrates, leading to the confirmation that the addition of APTES does significantly increase the stability and retention of the PSS:PEG film. More results are needed using the new cleaning and curing method in order to validate the consistency of these much improved results. Also, this testing was able to build upon previous testing by being able to consistently produce stable 75:25 PSS:PEG films. As noted earlier, the ability to produce a more negative charge in an aqueous environment is less likely to attract negatively charged foulants.

As seen in **Figure 2**, the surfaces of the PSS:PEG substrates with APTES appeared to be less uniform, with more spotting than the control PSS:PEG film surface. This is possibly due to dewetting of the surface caused by fluctuations in humidity during the spin coating process. When dewetting occurs, ethanol solvent evaporates and moisture accumulates on the substrate

surface leading to a non-uniform coating. The spotting becomes more prevalent when the polymer film is coated onto the dewetted surface. However, as seen in **Figure 3**, the increased stability can be seen as much more material remains on the surface of the samples containing APTES after rinsing with deionized water. In future experiments, it is recommended that the humidity is better controlled until a more uniform coating is present.

Figure 4 shows how the PSS:PEG on the APTES treated surface had less particle attachments than the controls. The decrease in particle attachment is due to the increase in surface stability and retention because each surface was rinsed after initial particle attachment. Protein adsorption testing resulted in little protein being absorbed by either control or APTES treated samples. This result demonstrates that the silane treated substrates were able to withstand an aqueous environment and still be able to provide fouling resistance.

Conclusion

In conclusion, the application of APTES, a silane coupling agent, did lead to increased stability and retention while displaying similar hydrophilicity and increased anti-fouling performance. However, optical microscope analysis showed some non-uniformity and surface spotting, especially with APTES treated samples, possibly due to dewetting of the films during the spin coating process. There were also some discrepancies within the collected data, possibly due to silane contamination in the vacuum oven. Further research must find ways to combat these issues such as by monitoring humidity and carrying out proper cleaning techniques in order to prevent contamination. If this research is continued successfully, this low fouling material can help reduce surgical and antifouling coating costs in a variety of fields including biomedical, maritime industry, food packaging, water and oil purification, and energy harvesting.

Literature Cited

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