

# IMPROVING THE HYDROPHOBICITY OF FABRICS WITH THE USE OF PHOSPHONIC ACIDS

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## ABSTRACT

This project examines the effect of phosphonic acid on the hydrophobicity of fabrics. Phosphonic acids provide an alternative to current hydrophobic coatings because of their ability to bond covalently with the oxide layer present on most surfaces. Phosphonic acids of various chain lengths were tested for their hydrophobic properties on a nylon-spandex blend, a versatile fabric used in water sports. Practical heating applications, such as the microwave, conventional oven, and iron were tested to determine the most efficient process to apply the coating. Results showed that phosphonic acids of all chain lengths increased the hydrophobicity of nylon, and the iron heating application provided the most efficient process.

## INTRODUCTION

### Overview

Synthetic coatings have been used on a variety of surfaces for water resistance and surface protection. Coatings that offer water resistance contain hydrophobic substances—non-polar molecules that have weak intermolecular forces with water. When water is placed on a hydrophobic surface, it will bead because cohesive forces (1).

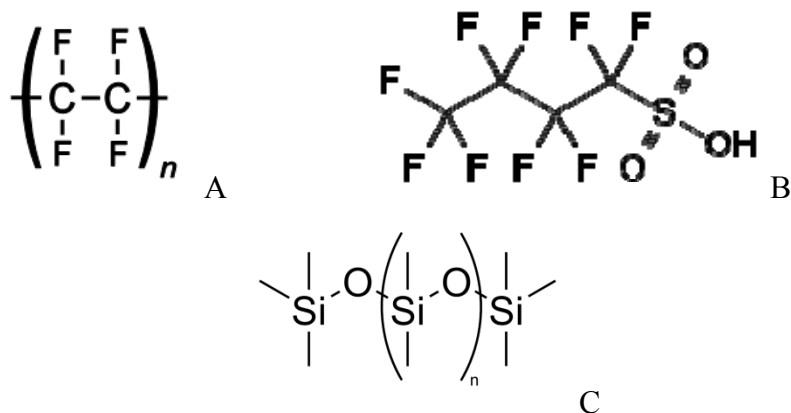
### Current Synthetic Coatings

Teflon®, Scotchgard®, and Rain-X® are some widely known examples of hydrophobic coatings. Teflon®, or polytetrafluoroethylene (shown in Figure 1A), is resistant to water, oil, and high heat. It is used in both household and industrial settings such as in nonstick cookware and factory machinery. For such applications, its low coefficient of friction is useful in creating non-stick, non-abrasive surfaces (2).

Scotchgard® is a brand of furniture and fabric protectant manufactured by 3M. The original formula was discovered accidentally in 1952, and 3M began manufacturing the product in 1956 (3). Currently, PFBS is a main ingredient in Scotchgard®, and its chemical structure is shown in Figure 1B. Scotchgard® is designed to be sprayed directly onto a fabric or piece of furniture. It forms a temporary bond with the surface of the object. This coating makes the object's surface water resistant, preventing it from accidental staining or water damage.

Rain-X® is an organic polymer primarily composed of polydimethylsiloxane (PDMS) (shown in Figure 1C). It is inert and acts only in a select few reactions under abnormal

conditions. When PDMS undergoes polymerization, it forms a uniform, hydrophobic surface that resists infiltration by aqueous solutions (4). Rain-X® (PDMS) is often sprayed on the window surfaces of automobiles in order to reduce visual obscurity when driving in rainy, foggy, or misty conditions.

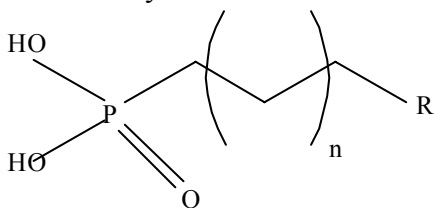


**Figure 1** 1A shows the polymer of tetrafluoroethylene, or Teflon®. 1B shows the structure of PFBS, the main ingredient in Scotchgard®. 1C shows PDMS in Rain-X®.

Despite the practical successes of these coatings, problems still remain regarding their safety and durability. In 2006, the EPA deemed Teflon® as a “likely” carcinogen (5), a danger of special concern since Teflon®, which does not form chemical bonds with surfaces, tends to flake off (6). Scotchgard® previously contained perfluorooctanesulfonamide, which was deemed by the EPA to be an organic hazard (7). This has since been replaced by perfluorobutanesulfonic acid, a substance which, while less dangerous in humans, still poses some concern (8). Chemically, Scotchgard® forms only a temporary bond with the treated surface and must be reapplied. Likewise, Rain-X® (PDMS) gradually loses its water-repellent properties through acidic corrosion and must be reapplied regularly. When the PDMS polymer is exposed to harsh external pressures, it can be chemically transformed into its monomeric constituents, which are much less hydrophobic than the PDMS polymer. Finding alternatives that do not degrade nor pose a threat to health is increasingly crucial as individuals rely more on synthetic coatings to change the properties of everyday objects.

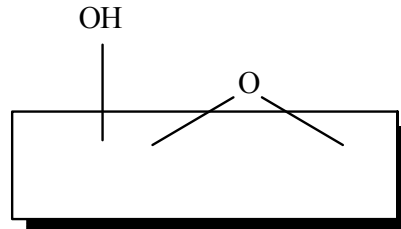
### Phosphonic Acids as Surface Coatings

Phosphonic acid coatings are seen to be a non-toxic, covalently bonded, more long-lasting hydrophobic coating (9). Phosphonic acids (PAs) are organic compounds that contain either C-PO(OH)<sub>2</sub> or C-PO(OR)<sub>2</sub> groups, as shown in Figure 2. The ability of PA to irreversibly and permanently attach to the surface oxide layer makes PA a desirable substance to research.



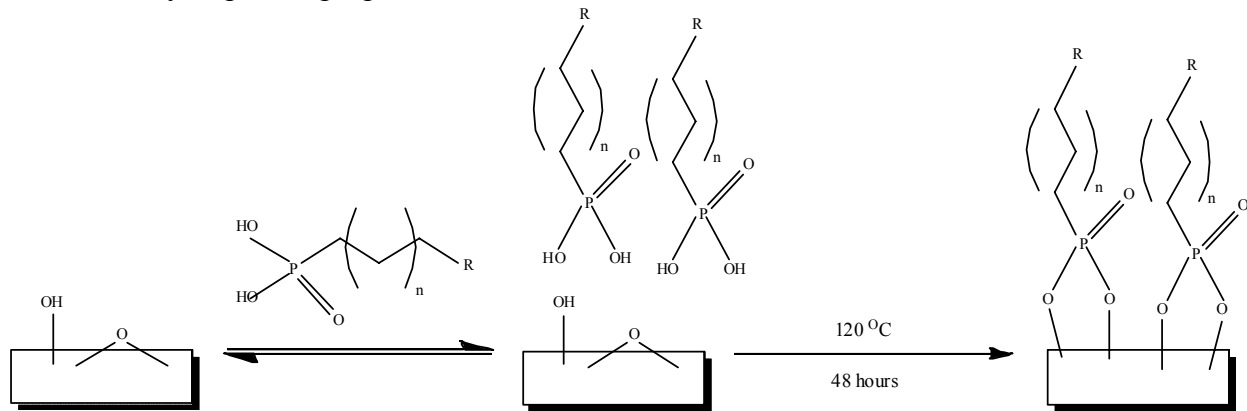
**Figure 2** PAs have a hydroxyl group on one side to bond with the substrate, and a carboxyl group.

An oxide layer is a surface characteristic of almost all surfaces that are in contact with oxygen. The oxide layers help protect surfaces from corrosion. The oxygen takes on two forms. As seen in Figure 3, the  $\mu$ -oxo groups consist of bridged oxygens that are largely unreactive (10). The hydroxyl groups are more reactive, though still limited at the surface. The lack of reactivity in both the hydroxyl groups and the  $\mu$ -oxo groups is why they are protective against corrosion, but this quality makes it difficult to bind substances to this surface. Some examples of common oxide layer forming surfaces include aluminum, titanium, copper, wood and ceramics.



**Figure 3** An oxide layer of the substrate in the experiments (e.g. glass, fabric).

PAs are unlike other coatings as other coatings simply adhere to the substrate physically. Other coatings are bound to the surface by means of adhesion or intercalation at the molecular level while PAs can covalently bond to the oxide layer of the substrate. The hydroxyl groups at the end of the PA chains form covalent bonds with the hydroxyl and  $\mu$ -oxo groups in the oxide layer through dehydration reaction. This leaves a self-assembled PA layer covalently bonded to the oxide layer, which interacts with materials on both sides of its chemical structure, as shown in Figure 4 (11). Leading from the PA is a tail of variable length and functionality which can bind to chemicals that would not directly bond to the surface. Long hydrocarbon chains in this tail bestow hydrophobic properties to the PAs .



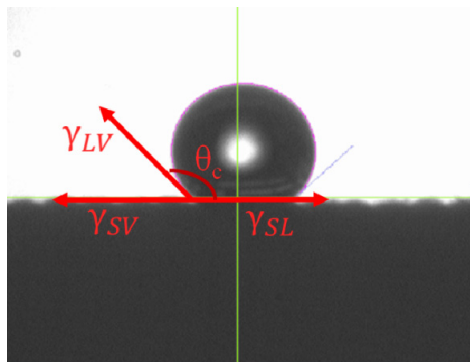
**Figure 4** Phosphonic acid undergoes dehydration in the presence of heat, covalently bonding to the oxide layer.

### Surface Energy

Surface energy measures the intermolecular bonds on the surface of a material, similar to surface tension for liquids. When water contacts a surface, the water forms droplets at a specific contact angle, as shown in Figure 5. Young's Equation (Equation 1) uses the contact angle formed by the water droplet and surface to calculate the solid surface energy (12):

$$\text{Eqn. 1: } \gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_c$$

Given the interfacial free energy of the surface and the liquid free energy of the water, the contact angle can be used to calculate the solid surface energy (12). A lower surface energy indicates higher contact angle and greater hydrophobicity, which will make it useful for real-world applications.



**Figure 5** Water beads on a hydrophobic surface at a specific contact angle.

SL = energy of the contact between the water and the nylon

SV = energy of the solid surface

LV = energy of the water molecule

### Fabric Substrates

Nylon, a group of polyamides made of repeating amide linkages, was developed by Wallace Hume Carothers for DuPont and introduced in 1939 at the New York World's Fair (13). The most common type of nylon is "nylon 6,6", made of hexamethylene diamine and adipic acid by a condensation reaction. The two component units alternate to form the fiber. Both hexamethylene diamine and adipic acid are compounds with six carbon backbones, which is why the fabric is called nylon 6,6 (14). Another basic nylon is nylon 6, which is known as polycaprolactam. Commercial nylon, such as nylon 6,10 and 6,12, contain additional methylene groups, which makes it more hydrophobic and suitable as a water-resistant material (13).

Spandex is a long-chain, synthetic polymer-based fiber consisting of up to 85% polyurethane and capable of stretching to 500% its dimensions. A long-chain polyglycol is combined with a stiff diisocyanate, which gives support to the flexible polyglycol fiber. The hydroxyl (-OH) groups on the polyglycol molecules react with the isocyanate (NCO-) groups on the diisocyanates molecules, and then a stabilizer is added to decrease vulnerability to light and heat. The solution is then spun into fiber (15).

Cotton is extremely absorbent and often used in towels and other products used to soak up liquids. Using cotton for this experiment provided an alternative comparison to the nylon-spandex blend (NSB) that was tested and coated for hydrophobicity in the experiment. The substrates used were an 85:15 nylon to spandex blend (synthetic fiber) and cotton (natural fiber).

### Purpose and Hypothesis

The purpose of this experiment was to optimize the bonding process of PAs to the surface of two main fabrics, NSB and cotton. Optimizing this process involved identifying the phosphonic acid with the chain length that yielded greatest hydrophobicity. Also, the most

effective heating method to bind the PAs was examined. Given the properties of PA, it was initially expected that the application of PA to the fabrics would yield an increase in contact angle and hydrophobicity. As a permanent, non-toxic substance, PA offers a promising alternative to current hydrophobic coatings, and the application of PAs to fabrics suggests that various surface types can be chemically transformed for particular needs and purposes.

## **PROCEDURE**

### Testing Hydrophobicity of Glass

One uncoated control group and seven different chain length groups of PA were tested. In all tests conducted, the acids (hexylphosphonic acid (HPA), octylphosphonic acid (OPA), decylphosphonic acid (DPA), dodecylphosphonic acid (DDPA), tetradecylphosphonic acid (TDPA), hexadecylphosphonic acid (HDPA) and octadecylphosphonic acid (ODPA)) were tested in triplicates. The seven chain lengths were tested on glass microscope slides. After cleaning with ethanol, both beakers and microscope slides were allowed to air dry. Beakers of a 0.002 M PA solution were prepared in a solvent of 95% ethanol and toluene (2:1 v/v). 7 triplicates were coated in PA solutions of different chain lengths and one triplicate was left uncoated for the control. The solution was evenly spread over the glass surface using a Mayer rod. To facilitate the dehydration step, air-dried slides were placed on aluminum foil and left for 48 hours in an oven at 120°C. Samples were removed from the oven and the hydrophobicity was measured using the contact angle test. The Ramé-Hart® Contact Angle goniometer was used to obtain average contact angle measurements from either side of the drop. Angles greater than 90 degrees are considered hydrophobic. Surface energy of samples was calculated using Young's Equation. Samples were then washed in ethanol to remove any unbonded PA from the surface. Contact angle measurements were recollected following the washing procedure to evaluate the presence of covalently bonded PA.

### Testing the Properties of NSB

A SPF50 brand swimsuit (85% nylon 15% Spandex® NSB) was first tested qualitatively for hydrophobicity by dropping water on fabric and examining the drop. The NSB also underwent heat tests using a heat gun, microwave, iron, and oven with temperatures at least high enough to speed up the dehydration synthesis reaction that binds PAs to surfaces. NSB was tested under the heat gun until melting at 800°C, 600°C and 400°C. Simultaneously, NSB samples were also tested in a microwave at high setting for 30 minutes. Finally, over the course of two days, samples were tested in the oven at 120°C for 48 hours. Samples of NSB also soaked in ethanol, toluene, and an ethanol-toluene solution at a 2:1 (v:v) ratio to check if any of these solvents had an effect on the fabric.

### Testing Hydrophobicity of NSB

NSB fabric samples were cleaned in warmed ethanol. Seven sets of triplicates were then dipped in each of the seven PA solutions, with one from each heating method left as a control. Using tweezers, samples were submerged briefly in PA solutions and left on aluminum foil to air dry. Samples were then either dehydrated using an oven at 120°C in an oven for 48 hours, in a

microwave for 5 minutes on high, or under an iron at Polyester setting for 10 minutes. Samples were divided so each chain length solution would be tested in each of the three heating methods.

The NSB samples were tested for hydrophobicity using the contact angle test. Samples were then washed in ethanol for increased hydrophobicity after cleaning and tested again.

#### Exposure Tests for Coated NSB Samples

The durability of ODPA bound to the NSB surface was tested in two common environments for swimsuit use: a washing machine and chlorinated water. Exposure to deionized water was also used as a control. For each heating method, samples were coated in triplicate with 0.002M ODPA or left uncoated. Each of these samples was measured for contact angles before and after the exposure tests to check for decreased effectiveness.

The three environments were simulated by using scaled down models. To simulate a washing machine's motion, samples were washed for 10 minutes in a 20 mL solution of Tide 2x Ultra with Bleach Alternative in water (3:500 v/v) with low heat and stirring. After washing, the samples were rinsed with the same magnetic stirrers in tap water for 10 minutes. Finally, samples were held under running tap water for one minute to remove any excess detergent that may have remained.

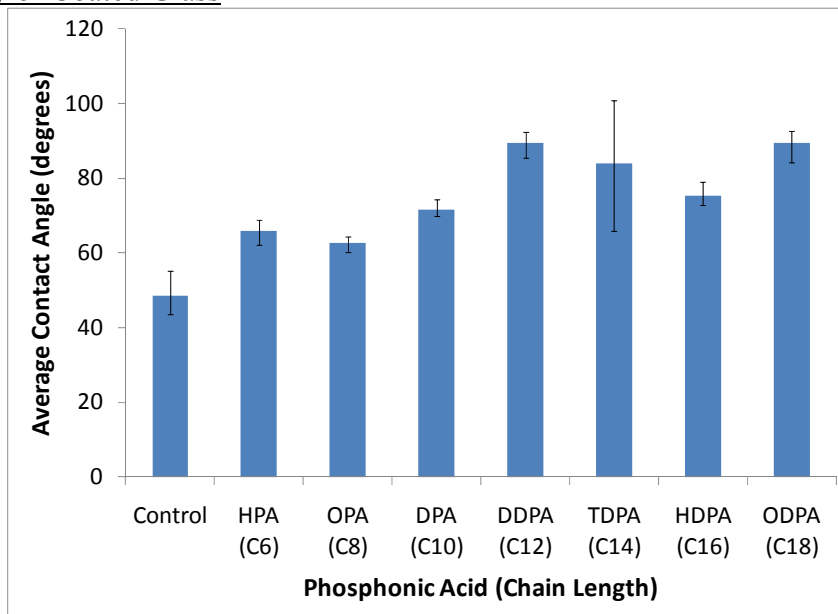
The samples were tested for exposure to chlorinated pool water by stirring in 20 mL of a 1.5 parts per million mixture of chlorine and water obtained from the Drew University Pool. For controls, samples were stirred for 10 minutes in 20 mL deionized water. All of the samples were tested by the Contact Angle Test after undergoing the exposure tests, and these measurements were compared to the corresponding ones taken before testing.

#### Coating of Cotton

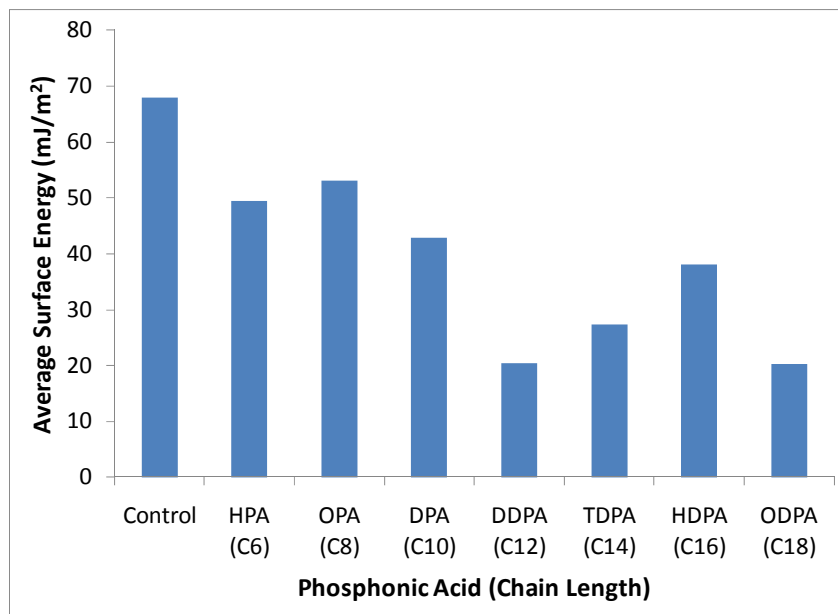
Two groups of three cotton samples were coated with the ODPA. ODPA was applied to samples of cotton fabric by submerging them in solution using tweezers. Samples serving as controls were also set aside. Three controls and three samples were dehydrated through ironing or microwave. The submerging and dehydration steps were repeated six times for a total of six coatings of ODPA on the cotton. Samples were then analyzed for hydrophobicity using the contact angle goniometer.

## RESULTS

### Hydrophobicity of Coated Glass



**Figure 6: Contact Angles on Coated Glass Samples.** The graph displays the average contact angles on glass surfaces that were coated via oven heating with PAs of different carbon chain lengths. Error bar=Range, n=3.



**Figure 7: Surface Energies on Coated Glass Samples.** The graph displays the average surface energy on glass surfaces that were coated via oven heating with PAs of different carbon chain lengths.

Figure 6 shows how the PA coatings on the glass surfaces caused significant increases between  $14.3^\circ$  to  $41.1^\circ$  in contact angle. Generally, the PAs with the shorter carbon chains yielded smaller contact angles on the glass and therefore caused less hydrophobicity than the acids with the longer carbon chains. The greatest increases in contact angle occurred on the glass coated with ODPA (C18), with an average contact angle of  $89.5^\circ$ , and DDPA (C12), with an

average contact angle of 89.4°. The increase in contact angles correspondingly caused a decrease in surface energy, according to Figure 7, meaning that the hydrophobicity of the glass samples increased after application of PA.

### Resistance of NSB to Heat

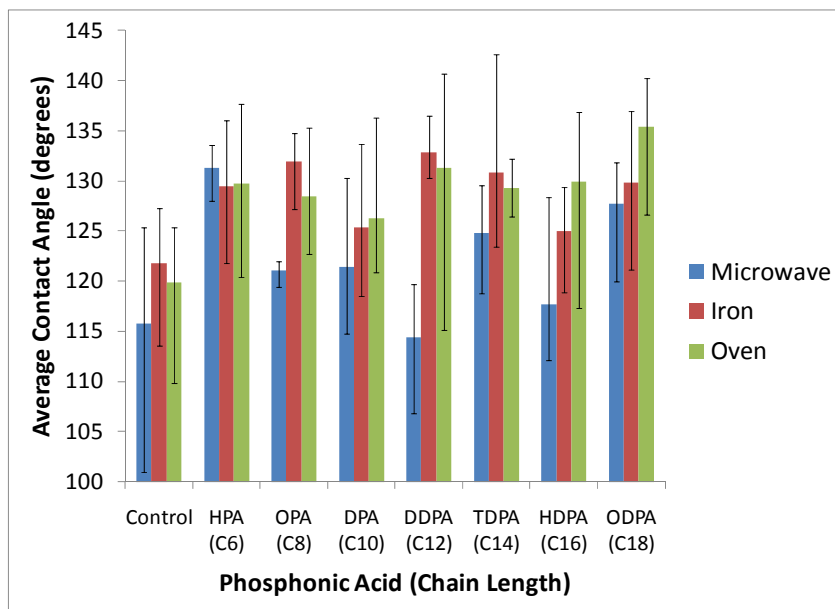
The heat gun, microwave, iron, and oven applications to the NSB determined whether or not NSB can withstand the heating methods and temperatures needed to induce the dehydration reaction for covalent bonding. Under a heat gun at 800°C, NSB samples melted within 16 seconds when the heat gun was placed four inches away. The samples melted in 26 seconds when tested at 600°C but took five minutes to begin melting at 400°C.

The other heating methods were tolerated by the NSB. After 30 minutes on the highest setting of a conventional microwave, the NSB samples showed no signs of melting. Samples under the iron did not melt under settings for nylon and silk but melted under the polyester, wool, cotton, and linen settings. They also remained intact after 48 hours in an oven at 120°C. After obtaining these results, the microwave, iron, and oven were selected as the three methods to test on coated NSB samples.

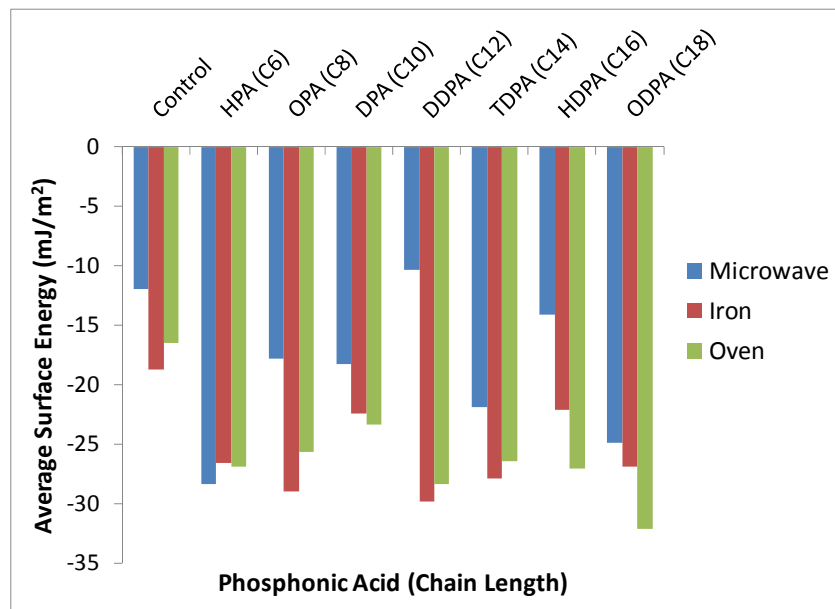
### Hydrophobicity of Coated NSB

The glass and heat resistance tests served as the benchmark for improving the hydrophobicity of fabrics, particularly NSB. When a drop of water was placed on the initial, untreated NSB surface, it resulted in a contact angle that, by observation, was clearly greater than 90°, showing that NSB is already a hydrophobic surface. Quantitatively, this observation was supported by measuring contact angles. The untreated NSB material has an average contact angle of 120.8°. Various heat treatments and application of PAs altered the contact angles. In general, the application of the PAs successfully increased the hydrophobicity of the already hydrophobic NSB. The newly coated NSB surfaces consistently yielded higher contact angles than just the uncoated NSB. There was variation in contact angle depending on the heating application used to covalently bind the PA to the NSB surface. Furthermore, the heating method itself appeared to affect the uncoated NSB as well, for the uncoated surfaces also yielded substantial deviation from 120° after application of heat.





**Figure 8: Contact Angles on Coated NSB Samples.** This graph compares the contact angles measured on uncoated NSB (control) and NSB coated with PAs of varying carbon chain lengths after three different heating methods. Error bar =Range, n=3.



**Figure 9: Surface Energies on Coated NSB Samples.** This graph compares the surface energies calculated on uncoated NSB (control) and NSB coated with PAs of varying carbon chain lengths after three different heating methods. Using Young's equation, the surface energy that results between an H<sub>2</sub>O molecule and the particular NSB surface was calculated.

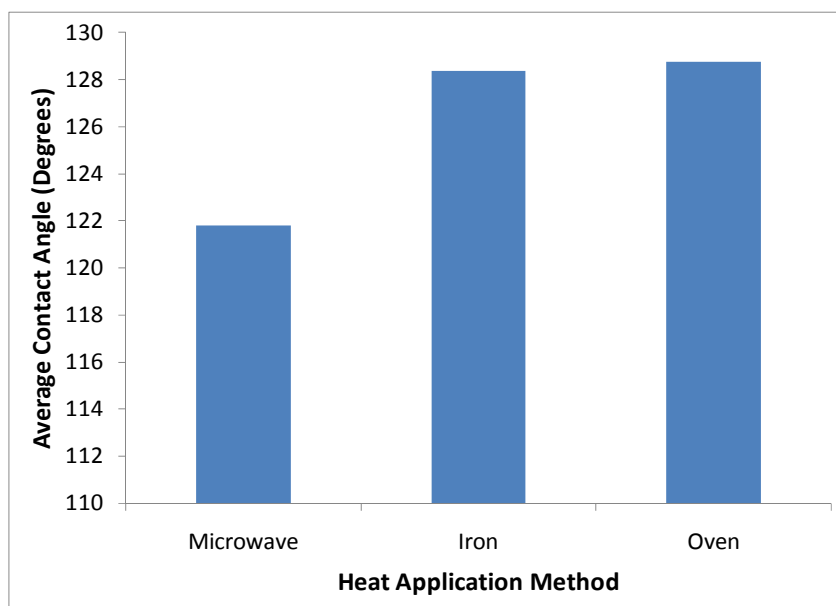
Figures 8 and 9 illustrate the increase in hydrophobicity when PAs are applied to NSB. Figure 8 shows that all three heating methods consistently produced an increase in contact angle from the control. However, all of the PAs did not produce equal changes in contact angle. Figure 9 depicts the same idea in terms of surface energy. Hydrophobicity is indicated by lower surface energy and higher contact angle. The coated NSB surfaces coated generally experienced a decrease in surface energy, but there was much variation among the varying chain lengths.

Among the samples treated by the microwave, all except one PA resulted in a higher contact angle than the control. Figure 8 shows that HPA (C6) and ODPA (C18) featured the greatest changes in hydrophobicity, with 15° and 12° increases, respectively. When using the microwave heating method, the DDPA (C12) caused a decrease in hydrophobicity instead of an increase. Microwaving the control caused a 5° decrease in contact angle than the contact angle on the pure, unheated NSB.

Among the samples treated by the iron, all of the NSB surfaces that were coated with PAs produced greater contact angles and lower surface energies than the control. The data for the microwave and iron illustrated approximately equal changes in contact angle and surface energy (Figures 8 and 9) from the control. Nevertheless, the ironing method yielded higher contact angle measurements, overall. Figure 8 shows that ironing the control sample seemed to produce no significant change from the unheated NSB because the contact angle of the ironed NSB is only 1° greater. The anomalous increase in surface energy for DDPA (C12) seen in Figure 9 for the microwave did not occur under the ironing method.

Finally, the contact angle and surface energy measurements under the oven method continued to parallel the iron and microwave results. The ODPA (C18) created the greatest increase in NSB hydrophobicity (15.6° increase), and this particular chain length has consistently been among the most effective in increasing hydrophobicity, according to Figure 8. Like the results for the iron method, all of the coated NSB surfaces produced an increase in contact angle and decrease in surface energy from the control. When dehydration was facilitated by the oven, the NSB coated with the DDPA (C12) also resulted in a lower surface energy, unlike the result obtained when the same PA was applied through microwave heat (Figure 9).

### Effectiveness of Heating Applications on NSB

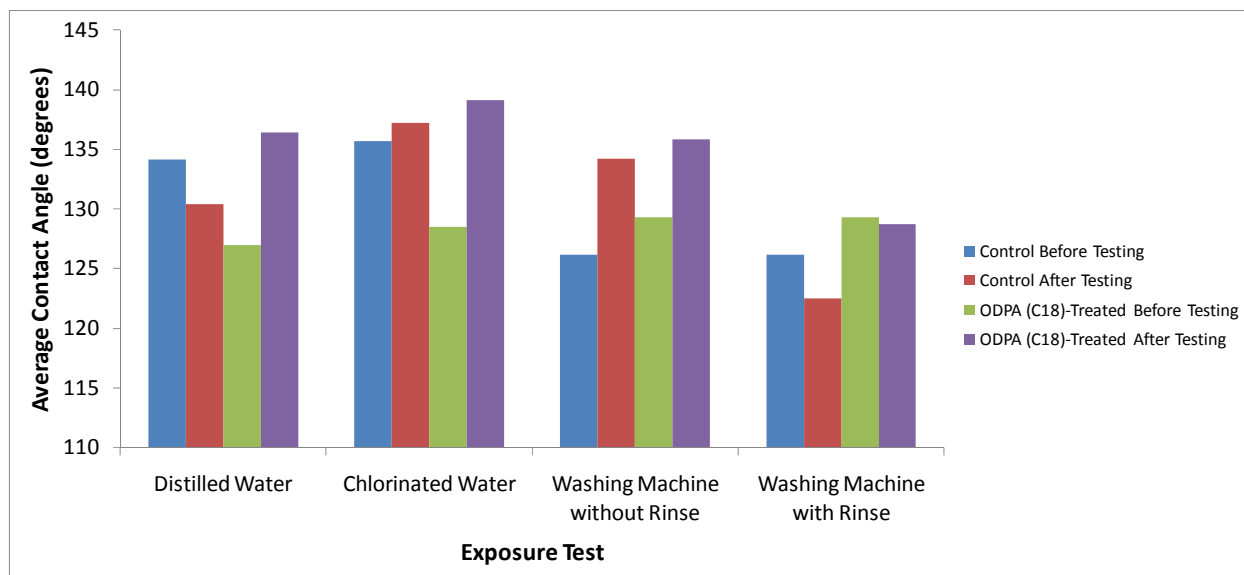


**Figure 10: Comparison of Heating Methods on NSB.** This graph displays the averages (grouped by heating mechanism) of the average contact angles measured for each phosphonic acid (HPA to ODPA) on the coated NSB.

The dehydration synthesis and binding of the PA, as the rate-determining step, was essential to improving the hydrophobicity. Figure 10 shows that average of all contact angles measured for each heating method to compare the effectiveness of each method. Figure 10 illustrates that the microwave yielded the lowest average contact angle ( $121.8^\circ$ ) while the iron and oven yielded approximately equal average contact angles ( $128.4^\circ$  and  $128.8^\circ$ , respectively).

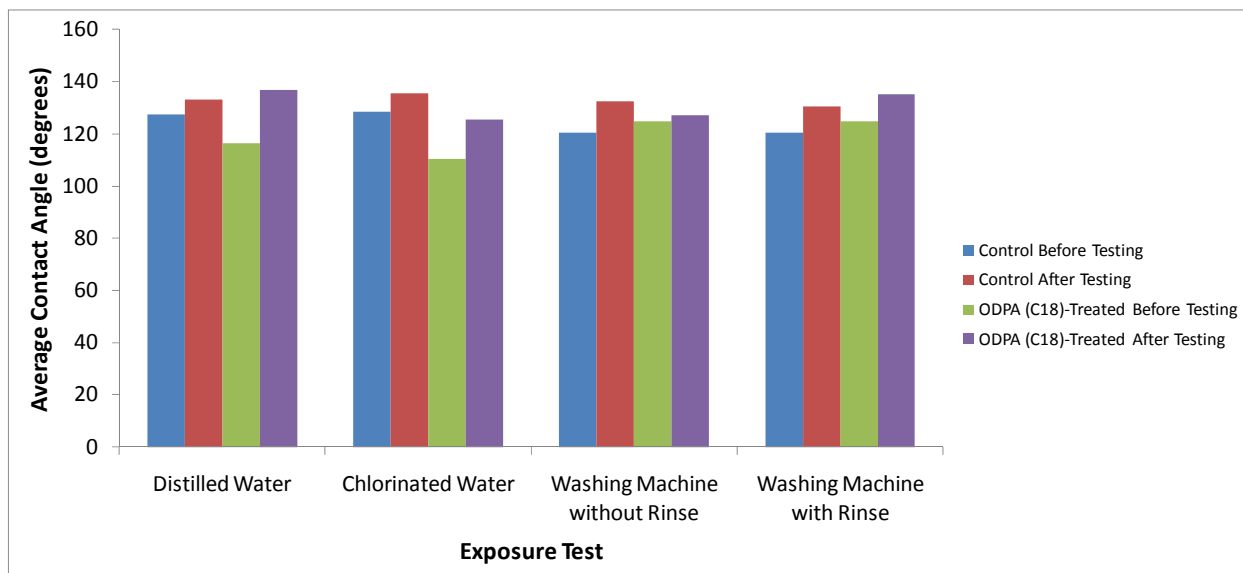
While the oven required 48 hours to complete the dehydration process, the iron required only 10 minutes and yielded approximately the same average contact angle.

### Exposure Tests on Coated NSB



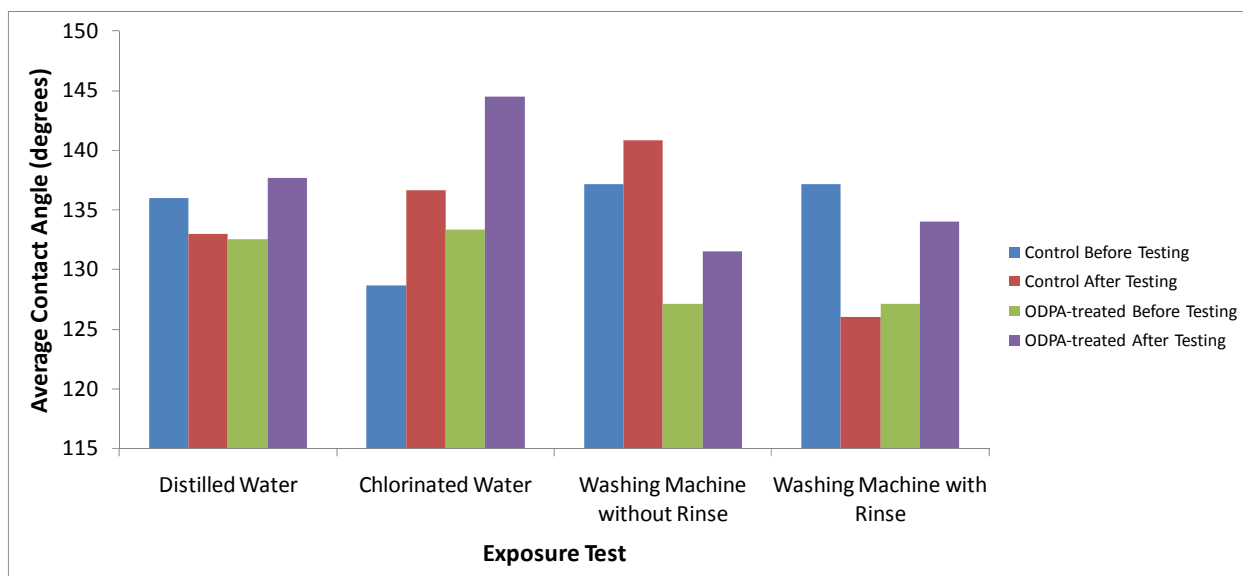
**Figure 11: Exposure Tests on NSB Coated by a Microwave.** This graph compares the contact angles measured on uncoated NSB (control) and NSB coated with ODDPA (C18) using a microwave before and after various exposure tests.

After each NSB sample was subjected to the exposure tests, contact angles were measured again and compared to contact angles measured before testing. Figure 11 shows that contact angles for the NSB control samples heated using the microwave increased after exposure to chlorinated water and the simulated washing machine without H<sub>2</sub>O rinse. However, they decreased after testing in distilled water and the washing machine with rinse. The NSB samples treated with ODDPA (C18) using the microwave method showed an increase in contact angles in all exposure testing methods except the washing machine with H<sub>2</sub>O rinse.



**Figure 12: Exposure Tests on NSB Coated by an Iron.** This graph compares the contact angles measured on uncoated NSB (control) and NSB coated with ODPA (C18) using an iron before and after various exposure tests.

Figure 12 shows that contact angles of NSB control samples heated using the iron method increased after all exposure tests. The NSB samples with ODPA (C18) applied using the iron showed the same trend, with average contact angles improving after each method of exposure testing.



**Figure 13: Exposure Tests on NSB Coated by an Oven.** This graph compares the contact angles measured on uncoated NSB (control) and NSB coated with ODPA (C18) using a oven before and after various exposure tests.

According to Figure 13, contact angles of NSB control samples heated by the oven increased after exposure testing with chlorinated water and the simulated washing machine without rinse and decreased after testing with distilled water and the simulated washing machine with rinse. The NSB samples using the oven method to apply the ODPA (C18) showed an increase in contact angle for all exposure tests.

### Hydrophobicity of Coated Cotton

The original samples of cotton were not hydrophobic at all and readily absorbed water. However, after six applications of ODP A (C18), this had changed drastically. When cotton treated with ODP A (C18) was microwaved, the average contact angle rose to 119.8 °. The average contact angle after ironing the treated cotton was only slightly worse, at 117.6 °.

### Exposure Tests on Coated Cotton

Although this large change in hydrophobicity was important, it was also necessary to test how well ODP A (C18) maintained its bond with the cotton when subjected to normal environmental conditions. The treated cotton was submerged in distilled water which was then stirred vigorously. Both the microwaved and ironed cotton samples saw an increase in hydrophobicity, with the contact angle of the microwaved cotton increasing from 119.8 ° to 121.4 ° and the ironed cotton increasing from 117.6 ° to 123.3 °. Next, the cotton was submerged in chlorinated pool water and stirred vigorously. The microwaved sample saw a decrease in contact angle from 119.8 ° to 115.7 °, but the ironed sample increased in hydrophobicity, from 117.6 ° to 123.4 °. Finally, the cotton samples went through a simulated washing machine. They were submerged into a mixture of water and detergent which was then stirred vigorously. In order to ensure the integrity of this test, the samples were later washed off with plain water in order to remove any residual detergent from the surface. Both samples became less hydrophobic after this test. The microwaved sample saw a relatively large decrease in contact angle, from 119.8 ° to 110.4 ° while the ironed sample saw only a small decrease, from 117.6 ° to 116.6 °.

## **DISCUSSION**

### Hydrophobicity of Coated Glass

The results on glass showed that shorter chain lengths were less hydrophobic than compounds with longer chains. This followed the initial hypothesis because longer, nonpolar hydrocarbon chains decrease the overall polarity of the molecule. Water is a polar substance and as a result repels the nonpolar hydrocarbon chain of the PAs, making the surface hydrophobic. Longer carbon chains increases the hydrophobicity of the fabric surface, making the contact angles of the water droplets larger. The pattern of surface energy observed at the various chain lengths further supports this reasoning and result. As a general trend, the surface energy decreases as the carbon chain lengths increase, which suggests an increased resistance to water.

After washing with ethanol and removing excess PA, the contact angles almost always increased. The surface energy decreased substantially as well. Therefore, rinsing with ethanol washes a significant amount of solution off of the substrate, making the surface more hydrophobic. This could be due to the removing of PA molecules that have not attached to the surface. Once these chains are cleaned off using ethanol, only the securely attached chains below are left. Together, these carbon tails create a more effective hydrophobic monolayer. HPA, however, is a notable chain due to its abnormal results. After the ethanol washing only HPA's hydrophobicity did not increase. This means that the other chain lengths exhibited greater

hydrophobicity after being rinsed, while the shortest carbon chain length decreased in effectiveness. The result may be due to its much shorter carbon chain length. It formed a closely packed monolayer, but because of the short carbon chains the excess lying on top of the layer actually served to help rather than detract from the hydrophobicity of the surface. This is why after washing with ethanol and rinsing away the multi-layer, the hydrophobicity decreased rather than increased.

Overall, the data on the glass demonstrate that DDPA and ODPa are best at creating a water resistant surface coating. The ODPa's effectiveness can be explained by its longer carbon chain, which would naturally repel the polar water molecules better. DDPa, however, did a better job of increasing the hydrophobicity of the glass even compared to TDPA and HDPA, which both have longer carbon chains. This is due to the structure of DDPa's carbon chains. The chains stack together in such a way that the tight organization creates a highly effective waterproof barrier that it is even better than the barriers created by the longer carbon chains TDPA and HDPA. After our preliminary testing, it is clear that DDPa and ODPa have the highest potential of being effective on the NSB material.

### Hydrophobicity of Coated NSB

Initial tests showed that the NSB was already hydrophobic, indicating previous application of a hydrophobic agent since untreated NSB has a reported contact angle of  $62.6^\circ$  (16). However, a surprising result was the differences in hydrophobicity after heating the fabric, without applying a PA. After ironing, the contact angles went up, but after microwaving and baking, the hydrophobicity decreased. These changes suggest that the heat and the way it was applied caused changes in the fabric that in turn influenced its hydrophobicity. Although interesting, this could also have contributed to the major variation in results that we saw throughout our tests, since this structural rearrangement could have interfered with the PAs that we were trying to test.

Our tests of the PAs yielded some surprising results as well. The microwave application method yielded positive results for all PAs except DDPa. However, the hydrophobicity of this molecule was among the highest when it was ironed and baked onto the fabric. Again, it seems likely that the way the heat was applied played a big part in the way the molecule bonded with the fabric and resisted water. It is surprising that DDPa resulted in the lowest contact angle when microwaved, yet had one of the highest when ironed or baked. Since microwaves rely on water content for heating, it is possible that the relative lack of water within the NSB prevented the DDPa from bonding completely with the fabric. More tests would be required to determine why microwaving the NSB was more successful with other chain types but did not work with an intermediate length like DDPa. This effectively proved that the method of application makes a difference in the molecule's ability to resist water.

ODPa, which has the longest chain length, was consistently a highly water resistant compound regardless of the application method. From this reasoning, it would make sense to assume that compounds like HDPA and TDPA (16 carbons and 14 carbons, respectively), which also have long carbon chains, would yield some of the higher results as well. It was puzzling, then, that DDPa, an intermediate chain length, yielded contact angles which were almost always

higher than those of longer PA chains. One possible explanation for this result is that a PA's hydrophobicity does not rely on the length of the chain, but on how well it can pack together on a surface. If a PA could seamlessly and uniformly bond to a surface, then the lack of gaps between the PA chains would shield the surface from any water, not allowing for much absorption. If this is the case, then DDPA and ODPA are probably the best PAs at creating a seamless layer across a surface. The inability of the other carbon chains to uniformly bond to a surface would also explain why the contact angles of HDPa and TDPA were lower than that of DDPa.

### Effectiveness of Heating Applications on NSB

These results lead to the conclusion that the oven facilitates in the dehydration step the most effectively, followed by the iron, and then the microwave, which does not create significant increases in contact angles. This inference was supported by a second set of measurements taken after washing the samples in ethanol to remove any excess PA not bonded to the surface. The oven samples still remained highest in hydrophobicity, and more importantly, suffered the least decrease in contact angle as a result of the washing, showing that more of the acid bonded to the surface when dehydrated with the oven than with the iron, and far more than with the microwave. This correlates to literary consensus, where the oven has proved the most reliable heating method for dehydrating PA (17).

While the oven gives better results, it takes 48 hours to dehydrate the sample, which is dramatically longer than the iron application, which takes only 10 minutes. By finding the optimal length of time for iron dehydration, the method could work just as well as the oven, but far more quickly. Even if multiple coatings needed to be applied to achieve the same result as the oven, the time involved would still be far less.

The microwave results were consistently low, sometimes even falling below the control, perhaps because the microwaving process degraded the original NSB surface by itself. The contact angle of the control itself was significantly less than the iron and oven controls, suggesting this conclusion. With the PA coatings, the contact angles increased, but were unremarkable in comparison to the oven and iron.

### Exposure Tests on Coated NSB

The exposure tests were performed on the ODPA samples and control samples in order to mimic and observe the effects of the everyday use of swimwear. The two exposure tests were in washing detergent and pool water, along with a distilled water control.

The hypothesis predicted that after these exposure tests the hydrophobicity of the samples would decrease slightly. This would have been for multiple reasons. First, the washes may have washed off any remaining PAs that had not covalently bonded to the oxide layer. In addition, the washes may have cleaved some of the covalent bonds between the surface and acid. Finally, the washes may have removed some of the oxide layer, removing the PAs with it.

Running the washing machine test on both the ODPA and control samples revealed a uniform increase in hydrophobicity. A likely cause is that some of the washing detergent was left

on the surface, acting as a hydrophobic coating. One of the main ingredients of washing detergent is a hydrophobic base to dissolve many chemicals (18). If this was left on the surface, it would have given the surface an unnaturally high hydrophobicity. After rinsing the surface with water, the hydrophobicity decreased to levels below the washing machine test. This substantiates that the fatty acids from the detergent increased the hydrophobicity of the surface.

The pool water test also showed similar results, in that there was also a significant increase in hydrophobicity after the exposure test. Similar to the washing machine test, the chlorine could have acted like second wash cycle in that it cleaned off the substrate, removing any materials off the surface such as dust, charged ions and other substances that could affect the hydrophobicity of the substrate. However, unlike the washing detergent, the chlorine would not have been able to deposit a hydrophobic layer on the surface.

The deionized water controls showed a uniform decrease in hydrophobicity. This result shows that it is most likely that substances within either the washing detergent or chlorinated water that are affecting the changes in hydrophobicity.

### Hydrophobicity of Coated Cotton

The cotton behaved differently from nylon in that it was originally a wetting surface. After being treated with ODP, the cotton became significantly more hydrophobic, achieving contact angles as high as 120°. This showed that ODP is able to make fabric surfaces more hydrophobic through the hypothesized methods. This result also gives more credibility to the smaller improvements in the nylon. Since ODP improved hydrophobicity so significantly in the cotton fiber, the results in the nylon are much more likely to be a result of ODP than errors.

### Exposure Tests on Coated Cotton

The effects of exposure tests on the cotton varied. For the distilled water control, the hydrophobicity increased. However when subjected to the washing machine and pool tests, the hydrophobicity decreased slightly. The distilled water most likely washed off debris (similar to how the washing machine and pool tests did before) and increased hydrophobicity. However the washing machine and the pool test for the microwave decreased the hydrophobicity of the cotton, possibly because of the cleaning agents in both. This explains the discrepancy between the nylon durability results and the cotton ones. Since the nylon was hydrophobic to begin with, each ODP molecule would have had a smaller effect on the hydrophobicity of the surface than on the cotton, as it was a wetting surface to begin with. Thus the washing machine and pool water may have damaged comparably the same amount of ODP, but this same damage would show a more profound change in the cotton surface.

## **CONCLUSION**

### NSB

This project's use of NSB as a substrate posed some problems in terms of the effects of the heating method on the fabric. The control samples demonstrated that microwaving and



baking the NSB worked to reduce its hydrophobicity, which could be the reason behind the variations among the results. However, the application all of the chain lengths but DDDPA yielded an increase in hydrophobicity, with baking and ironing being the most effective methods of application. Given that fact that ironing is effective, time-efficient, and seems to have no effect on the fabric itself, it seems to be the best method of application.

### Exposure Tests

The exposure tests that were run gave somewhat confusing results. In all but the control test (deionized water), hydrophobicity increased following the test. It is possible that something in the pool water and detergent solutions stuck to the fabric and made it more hydrophobic or that errors in measurement or experimentation occurred. However, there is no concrete evidence to prove this; further testing is needed to confirm.

### Sources of Error

It is important to note that some of the data may appear inconsistent due to experimental sources of error. Though our numbers showed an increasing trend in contact angles, they may appear statistically insignificant because of our small sample size. The 24 hour time constraint limited the number of samples that could be tested. The small sample size of three made it difficult to see a clear trend because of natural variation inherent in any experiment. Therefore, the three week limit was a critical factor to the outcome of the experiment.

While testing, the goniometer was not always consistent in its readings. Because the machine is designed to calculate on flat surfaces such as metal and glass, when the NSB curled, the contact angle reading would not accurately measure the angle at which the droplet contacted the surface; it would measure the tangent line to the curvature of the fabric. The cloth-like nature of the NSB made it also difficult to get an accurate reading because if the angle was not measured immediately after the droplet was put on, the droplet would begin to sink into the fabric. The sensitive nature of the goniometer made it difficult to collect extremely accurate data, which is why the same carbon chain was tested multiple times.

To figure out which heating applications would work best, preliminary tests were conducted on the NSB itself. By heating the NSB material with a microwave, heat gun, iron, and oven, we were able to form a rough idea of what heat settings to use to prevent the NSB from breaking down. However, when the NSB with the ODPA was heated, there is a possibility that some of the NSB broke down, or the Spandex® material reacted with the ODPA interfering with the hydrophobicity, since a polymer coat would form on the surface. Another variable is the thoroughness in which the exposure tests were conducted. As shown in the results, washing the NSB fabric coated with ODPA actually increased the contact angle thereby making it more hydrophobic, even though washing it should have removed some of the ODPA from the fabric. This may be attributed to the washing detergent being left on the fabric after it was washed. If the soap was not thoroughly rinsed off, the soap would form a coating on the surface of the fabric and the hydrophobic tails would repel water when the contact angle test was applied.

On the other hand, the opposite may have been true as well; had the coated NSB not been thoroughly heated or rinsed, the calculated surface energies would not accurately reflect the hydrophobicity of the NSB.

### Future Work

Time limits restricted the amount of research done, but future projects could be done to confirm and expand on ideas brought up in this project. For example, more samples per test or application method would further substantiate the conclusions made in this paper. Also, testing more chain lengths to find out which one works best on the NSB would maximize hydrophobicity. In this experiment, only the chain lengths that worked best on the glass (HDPA and TDPA) were used. Further durability tests to show how the PA performs after being exposed to other conditions such as stretching and erosion could also be performed. In addition, multiple coatings could be applied to the same sample to test for possible increases in the hydrophobicity of the surface following successive treatments.

Other experiments can also be done to expand this research. For example, substances with the same phosphate base but different R groups can be tested, as can other carbon chain lengths. Different fabrics or other substrates could be used to further test PA's effectiveness and binding abilities.

This research also has real-world applications. A new generation of durable, low-resistance swimwear which does not absorb water could be made using this protocol. This method is fast and easy to carry out, so PA in solvent could be sold for at-home application to most surfaces, as the heat sources that can be used to carry out the reaction are common household objects.

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