

CAN WE DEVELOP THE NEW TEFLON? DEVELOPING COATINGS AND LOOKING AT SURFACE MOLECULAR DYNAMICS

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ABSTRACT

Teflon has become one of the most widely used compounds in industry since its invention in 1938. Several problems with Teflon, however, have arisen in recent years including an EPA report labeling Teflon and other fluorocarbon compounds as potential carcinogens.

Octadecyl-phosphonic acid (ODPA) has shown to be a potential replacement for Teflon; it covalently bonds with the oxide surface in a self-assembled monolayer, exhibits the same properties as Teflon and is one of the few compounds that can bond with the titanium oxide surface. In this study, ODPA was bonded onto silicon dioxide surface through different methods including the T-BAG—Tethering by Growth and Aggregation—method, mayer rod application, drain submersion, drip method and spray method. In addition, different heat application methods were experiment with including the heat gun, iron, infrared light, ultraviolet light, and oven. The efficacy of the application methods were determined by contact angle measurements using water drops. Mayer rod application with iron heating proved to be the most effective method of application. To support the results and to gain a better understanding of the surface chemistry, computer models were developed which simulated the phosphonic acid molecule and the oxide surface. It is advised that further studies be conducted in this field to optimize the efficiency of coating surface layers.

Keywords: self-assembled monolayers (SAM), surface coatings, octadecylphosphonic acid (ODPA), oxide surfaces, contact angle, T-BAG (Tethering by Growth and Aggregation)

INTRODUCTION

Sold commercially as Teflon, polytetrafluoroethylene (PTFE) has become one of the most widely used chemical compounds in the modern world. Due to its unique properties, Teflon can create a highly hydrophobic surface with a low coefficient of friction, making it essential in the fields of chemical engineering, space engineering and medical industries, where non-stick, low friction surfaces are frequently required. Highly inert, Teflon reacts with only a handful of rare metals under abnormal conditions. Though it has been labeled as a potential carcinogen by the EPA, Teflon has continued to serve as the non-stick surface of choice.

Advantages of PTFE

The carbon backbone of the Teflon chain is fluorinated. Due to its symmetrical arrangement, the polymer is generally non-polar. As a result, no net charge prevails upon the Teflon chain [1]. The strength of the intra-polymer bonds inhibits reaction with most chemicals. Due to these bonds, PTFE is un-reactive when exposed to UV light, allowing it to be used upon surfaces exposed to the sun. Due to the strength of the carbon-fluorine and carbon-carbon single bonds, appreciable thermal energy must be absorbed by the polymer before thermal degradation. The most well-known property of Teflon is its high hydrophobicity. For Teflon to absorb water, the surface must remain wet for an extended period of time to allow for physical and chemical bonds to be created between PTFE and water. If wetting were to occur, the hydrogen bonds between the water molecules would have to be disrupted by the attraction between the PTFE chain and water.

Problems with Teflon

Though Teflon was at one time hailed a marvel of the modern chemical-industrial world, new problems with the polymer have arisen in recent years. Teflon is only physically bonded to the surface through intermolecular forces—no bonds are made between the surface and the Teflon molecule. The polymer coating does not consist of a one molecule thick layer, but a several hundred nanometer thick layer of polymer. This coating wears over time, giving rise to byproducts that are biologically harmful [4].

The EPA has recently begun investigations into these harmful byproducts of Teflon and their effects on the human body. Studies have found trace levels of perfluorooctanoic acid—PFOA, a basic component in the manufacturing of Teflon—in the blood samples from across the nation. Lab rats and mice exposed to much larger amounts developed brain tumors [1]. The EPA has now declared PFOA a potential carcinogen in humans.

Flouride has been identified as a residue of toxicological concern. Compounds which are more than approximately 52.8% fluoride are shown to act as free fluorides which are ubiquitous in the air, soil and water. Fluoride has also been identified as biologically harmful and has been identified as a potential carcinogen by the EPA. As a result, fluorinated compounds are carefully regulated by the EPA and limits are placed on the amount of fluorine allowed in commercial products [5]. Teflon exceeds what the EPA has deemed acceptable amounts but is still produced in large amounts due to its importance in industry. However, it is crucial that a new non-stick, hydrophobic surface be developed.

Dynamics of Oxide Surfaces

An oxide surface is any surface that is protected by a covalently-bonded thin-coating of oxygen. Glass, SiO_2 , is a common oxide surface. This oxygen takes one of two forms: μ -oxo groups and hydroxyl groups. The μ -oxo groups resemble ester bridges found in organic chemistry. Oxygen is bonded to the surface at two separate sites and is largely unreactive (Figure 1). The hydroxyl groups are

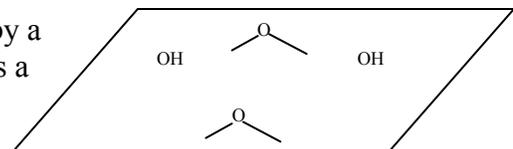


Figure 1. Oxide Surface

more reactive due to the fact that the oxygen is only bonded to the surface at one site. Reactivity of these oxygen groups varies between metals, with ZrO_2 being fairly reactive while TiO_2 is mostly unreactive.

The Self-Assembled Monolayer—SAM

A self-assembled monolayer is a thin film, normally less than 10nm in thickness, assembled spontaneously due to intermolecular and intramolecular forces. The most ubiquitous example of the self-assembled monolayer is found in cells in the phospholipid bilayer. Only one molecule thick, the phospholipid bilayer provides the cell with a versatile and pliable boundary. SAMs can be either physically held to the surface by electrostatic forces or be bonded chemically to the surface. The major problem with physically bound monolayers is their inability to withstand external forces of removal such as water and air [3].

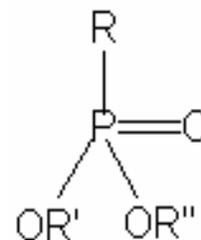


Figure 2. Phosphate

Phosphonates and Phosphonic Acids

Phosphonates are a class of organic compounds with a phosphorous doubly bonded to an oxygen, singly bonded to an R-group and singly bonded to two oxygens. The latter oxygens are bonded to an R'-group and an R''-group (Figure 2). Phosphonates have three main properties: they are strong chelating agents—chemical substances which cause the formation of ligands—

they inhibit crystal growth, and are stable under most harsh conditions. The toxicity of phosphonates to organism is fairly low compared to other organic compounds due to its ubiquity in the biological world [1].

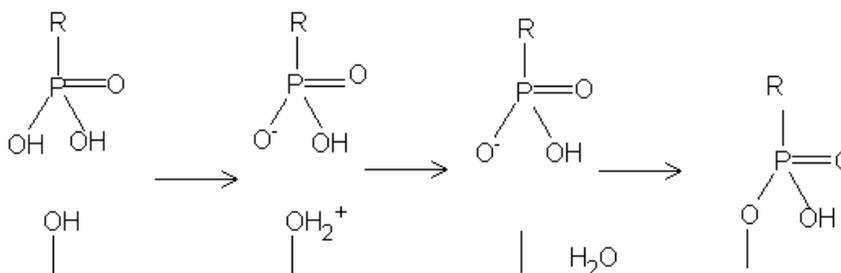


Figure 3. Dehydration Reaction with hydroxyl group

Reaction Mechanism

The SAM is stable in aqueous environments as well as resistant to heat and various pHs. In order to create a hydrophobic surface, alkyl chains can be attached to the phosphorous [9]. The interaction between phosphonic acid and the oxidized surface is a simple dehydration reaction. In the simplest case, the phosphonic acid donates a proton to the hydroxyl group, protonating it. The protonated hydroxyl group breaks off to form water while the ionized phosphonic acid attaches itself to the surface (Figure 3).

In the case of the μ -oxo group, the reaction process is slightly more complicated. The phosphonic acid molecule donates a proton to the μ -oxo group, protonating it. The μ -oxo bond breaks, forming a hydroxyl group and create an “electron vacuum.” The ionized phosphonic acid bonds to this electron vacuum,” creating a covalent bond with the surface (Figure 4).

The Project

The goal of this research project is to find a new method to improve the application process and efficiency of ODPA to an oxide surface by either increasing the rate of reaction or improving the even distribution of the ODPA molecules.

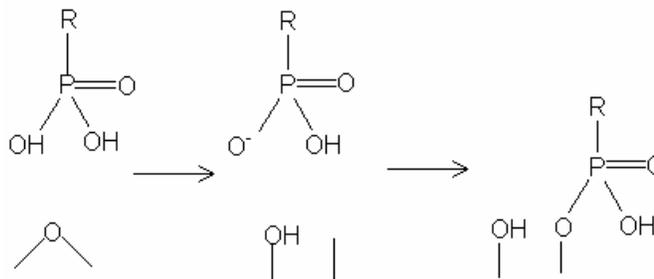


Figure 4. Dehydration reaction with μ -oxo group

MATERIALS AND METHODOLOGY

The standard procedure for chemically bonding ODPA to surfaces involved two main stages. First, ODPA was dissolved in a 2:1 Ethanol:Toluene solution so as to form a 0.001 M solution. Using one of many variable methods, the ODPA from the solution was physically bonded to the surface of a small standard glass slide, mainly by evaporative forces. Then the ODPA was chemically bonded to the surface by one of several different methods of heat or radiation.

The original method of coating glass, the T-BAG method, has been proven to be consistently the most effective and comprehensive coating technique. In this procedure, the slides are immersed in the Ethanol-Toluene solution and allowed to evaporate for 24 hours, forcing the ODPA to physically bond completely to the oxide surface. To chemically bond the ODPA, the glass slide is placed in an oven at 120° C for 48 hours. This method requires an excessive amount of time but was used in the experiment as a standard of comparison for the other procedures.

For some tests, a pre-treatment was performed before the physical bonding component. One variable involved washing the slides with ethanol to allow for a cleaner surface for ODPA application. Other slides were dipped in 5 M sulfuric acid to corrode the glass and create more alcohol groups on the oxide surface. Theoretically, this would allow for more ODPA to physically bond by increasing surface area.

Several modes of evaporation were explored. In what was dubbed the “spray method,” the solution was applied to the glass surface using a household spray-bottle and then left to dry. The Mayer Rod (a metal bar with micro-crevices) was used to roll over the surface and create a thin film of solution after the surface was either sprayed or dripped with a pipette with the ODPA solution. In another method, the slide was submerged in a trough of solution with only a thin film of solution covering the surface. A rubber tube was drawn across the surface, dragging a small amount of solution over it and leaving behind physically bonded ODPA. In the “drain method,” the solution was drained past the slides in a funnel allowing it to evaporate quickly.

The methods of chemically bonding the ODPA to the surface involved heat or radiation. The slides with ODPA physically bonded were placed in an oven and heated for 48 hours to compare to the other heating methods. For each physical bonding method, many heating methods were performed for different amounts of time. Slides were either placed under a UV lamp, an

Infrared Radiation lamp, a heat gun, or exposed to direct sunlight. An iron was also used for some slides to force chemical bonding. To further test for greater efficiency of methods, some full procedures, physical and chemical bonding components, were repeated several times on slides and tested after each repetition. To speed up the chemical bonding, sulfuric acid was tested as a dehydration reaction catalyst. It was added to the solution of ODPA in a small concentration for physical bonding so it would be present during chemical bonding.

The efficacy of the various methods used to create a non-stick surface was ultimately tested using a Ramé-Hart Contact Angle Goniometer, which measures the contact angle created by a droplet of water on a surface; in our tests, we placed 4 droplets of water on each glass slide and measured the contact angle between the drop and surface. A higher contact angle indicated a higher degree of hydrophobicity of the surface.

PROCEDURE

Method I: The “T-BAG”

In past studies, it was shown that the original method of coating the glass slide via evaporation was a highly effective method for application of SAM's. This method, known as the “T-BAG” (Tethering By Aggregation and Growth) method, involved placing a glass slide into a beaker containing a 0.001 M solution of octadecylphosphonic acid (ODPA) in a solvent of ethanol and toluene, in a ratio of 2:1, respectively. Once the solvent had evaporated and the ODPA had physically bound to the glass surface, the glass slide was heated in an oven for 48 hours to allow for chemical bonding.

Method II: The “Drain”

The method of physical bonding by evaporation in the T-BAG approach is effective, but not very time-efficient. In order to expedite this method, a drain-down system was devised. At the top of the apparatus, a funnel was used as the locus of evaporation. The funnel was connected to a stop-cock either directly or through a small amount of tubing. The drain-rate of the stop-cock was set to an initial rate of 5 mL/minute, which emptied the funnels in around 40 minutes. Thus, evaporation occurred as the water level slid down the glass. An additional benefit of this system is that the solution can be recollected and used again. Because the quantity of ODPA in the solution is approximately one thousand-fold the amount necessary to coat a surface, the same solution could be poured back into the top with only negligible loss of efficacy. Furthermore, unlike most other quick methods of physical coating, both sides were layered at once because the slides were still immersed in the solution.

Once this control was established, two variables were introduced. The drain-rate was tripled to test if the process could be speeded up even more. The second variable was created when results from the control indicated that the bottoms of the slides were being coated far worse than the top. It was hypothesized that the slides were being removed from the apparatus too quickly and therefore the lower end didn't have any solution evaporate on it. Therefore, the method was revised and the slides were allowed to air-dry in the apparatus for 5 minutes after dripping has stopped.

Various methods were used for drying the drain-test slides to allow for chemical bonding. Slides were exposed to: direct sunlight, an ultraviolet lamp, a microwave oven, and an infrared lamp. One slide in each case was exposed for 10 minutes, while the other was exposed for 20 minutes. The slides that were left to sit for 5 minutes were also subjected to the same drying methods.

Method III: The “Spray”

In another physical application method, the effects of spraying the solution on the glass slides were tested. So as to simultaneously evaluate methods of heating and provide several areas of comparison, three slides were simply sprayed once and placed under the IR lamp for 10 minutes; two other slides were sprayed once and heated in an oven for 48 hours. This procedure was repeated for 5 more slides with the entire method repeated. The effects of pre-wetting the glass slides with ethanol before coating them with the octadecylphosphonic acid solution were also tested. After the solution was applied, the slides were heated with infrared radiation for 10 minutes or in the oven for 48 hours. Multiple slides with identical processes were tested so results would be reliable. After this process, another set of slides was first treated with sulfuric acid and then followed the same steps as the previous set. In theory, the strong acid would create a better bonding surface for the ODP.

In another series of experiments, 12 slides were tested for the effectiveness of spraying the ODP solution and then using the Mayer rod. All slides were first washed with water and then spray-coated solution. A Mayer rod was used to smooth the surface to a very thin layer and spread out the ODP. After this, the effects of three different chemical bonding methods were found by testing 4 slides on each technique, 2 for 10 minutes and 2 for 20 minutes. Four slides were placed under an IR lamp and heated, four slides were held under a heat gun on high power, and the last four slides were set up under a short wave ultra-violet light lamp.

Finally, after the chemical procedure had been completed for each method, the repetition of these methods on the slides was tested. The slides were recoated using the same physical bonding method of spraying and rolled with the Mayer rod. Then the slides were placed under their respective lamps for the same time interval to allow for chemical bonding. These full procedures were repeated twice on one slide from each slide pair, as a control. The other slides in the pairs that were under their lamps for ten minutes underwent their specific treatment nine times, while the ones under the lamps for twenty minutes were treated six times altogether.

Method IV: The “Rod”

Another part of the procedure involved saturating the surface of the glass slide with ODP solution using the spray bottle, ensuring that no part of the surface was left uncoated. The Mayer rod was then dragged across the slide from top to bottom. Dragging the rod left a thin film of ODP solution on the slide. The slide was then placed on the lab table and the iron was applied on the cotton setting, moving it back and forth across the slide while applying pressure for five minutes. This procedure was then repeated twice more to ensure a comprehensive coating. The effects of washing the slides after treatment were also tested; one slide was rinsed with water and one was rinsed with ethanol after treatment. Three slides were also dried using the IR lamp 4 times instead of the iron. In another procedure involving the Mayer rod, several

different heating methods were used: IR radiation, a heat gun, and an oven. Another procedure involved varying the initial conditions of the slide: no pre-wetting, pre-wetting with solvent, and pre-wetting with sulfuric acid. The experiment was performed again; however, it was different from the original approach in that the end of the slide from which the ODPA was moved with the Mayer rod was changed, allowing one end of the glass slide to have a better coating than the other. This was done to allow a more even coating to develop on the surface of the glass. The effects of sitting a slide in a water bath for 5 minutes and using ethanol to remove any ODPA that was not chemically bound to the surface were also tested.

Computational Simulation

Computer modeling and simulating was used to better understand the actual molecule. With this knowledge, one could improve its structure, its applications, and the methods of applying it to glass surfaces. The computer program, Visual Molecular Dynamics (VMD), allows one to analyze the chemical bonding of ODPA solution with glass on the molecular level as well as simulate ODPA under varying conditions. By attaching it to a glass surface and adding water to its environment, one discovers why it is hydrophobic and what other potential interactions it has with water molecules. Since ODPA is not stable in all conditions, raising the temperature will reveal the maximum stress that the molecule can endure while retaining its properties. With this information, certain applications, such as those using high temperatures, can be ruled out.

A key property of the molecules is the interactions of their chains with one another. They pack tightly to form a seal that prevents water from interacting with the surface beneath. However, other variations in molecular structure and application to the surface may produce more effective results. The end group of the ODPA, a methyl group, defines many of its interactions. But, there are many other end groups that could be tested to increase the hydrophobic property.

VMD interprets Protein Data Base (PDB) files and provides the arrangement of the desired residues, thereby presenting the molecule. Once the molecule was constructed, it was manipulated for closer analysis of the bonds and spatial coordinates. The challenge was the parameterization of the molecule. Before this attempt, the octadecyl phosphonate had never been constructed. Because of this, the program failed to recognize the bonding of several residues. Thus, a similar system was analyzed that consisted of alkyl phosphones attached to a silicate surface. This model was useful in simulating the desired ODPA parameters. The ODPA model was constructed with the following criteria: rigid surface, oxygen binding sites, one-dimensional surface, and adherence to the laws of chemistry.

RESULTS

The T-BAG method, the industry standard and our standard of comparison, had a consistent contact angle of 95°.

Drain (15 min)

The six slides coated by the drain method for a duration of 15 minutes generally showed poor results (Figure 5). Five out of six slides had average contact angles less than 80°. Out of these five, the two which showed the best angles were heated by the heat gun after being coated by solution. The angles were 76.8° for 10 minutes of heat and 68.5° for 20 minutes. This is interesting because we expected the longer duration of heat to increase the effectiveness of the solution's bond to the glass surface. The results, however, contradict

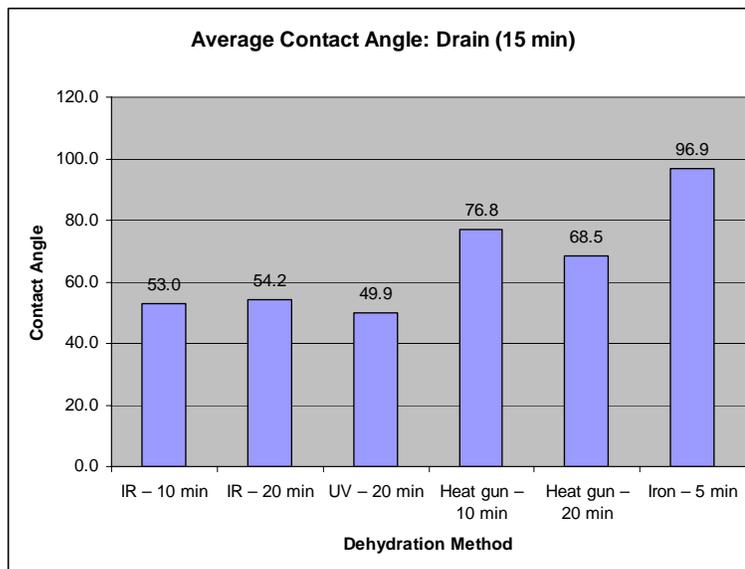


Figure 5. Avg. contact angles for 15 min. Drain

this hypothesis and more tests should be done to see if this remains consistent. Although the resulting contact angles were not good for a hydrophobic surface, they were significantly better than the angles of the slides that were treated with either UV or IR radiation. The average for these three was about 50°. The sixth slide had a high contact angle (96.9°) in comparison to the others and was heated using an iron for just five minutes.

Drain (45 min)

Another set of slides received the same drain coating method except these eight were treated for 45 minutes instead of 15. This extended length of exposure to the solution seemed to have significantly improved the hydrophobic quality of the surface. In contrast to the last set, four of these eight slides had contact angles *greater* than 80°. The iron was not tested on these slides so the highest contact angles came from the slides that received UV radiation. Again, the results were rather puzzling. The slide treated for only 10 minutes had an average contact angle of 88.8°, more than the 82.1° angle of the slide treated for 20 minutes. Interestingly, the other three heat sources also showed this result of slightly higher contact angles for slides treated for 10 minutes rather than 20.

Drain (45 min) - Repetition

Next, the five most hydrophobic slides from the previous test underwent a second repetition of their process (Figure 6). This time, however, they were only drained for 15 minutes; not 45. The three worst, the two microwave slides and Sun-20 min, did not receive this treatment. Originally, these slides were, in order from best to worst, UV-10 min, IR-10 min, UV-20 min, IR-20 min, and Sun-10 min. After they received their second coating and heat treatment, the order changed to: IR-10 min, UV-10 min, UV-20 min, IR-20 min, Sun-10 min. In both cases, the Sun seemed only to do a mediocre job and the bond angle went up by less than one degree after the second coating. The UV slides also showed results almost equal to those from the first

coating. The UV-10 min slide actually showed an average contact angle slightly lower on the second repetition. However, this could be due to an unevenly coated surface on either the first or second slide. Under IR, the 10 min slide improved by more than 10° while the 20 min slide hardly improved at all. These results are visible in the following graph.

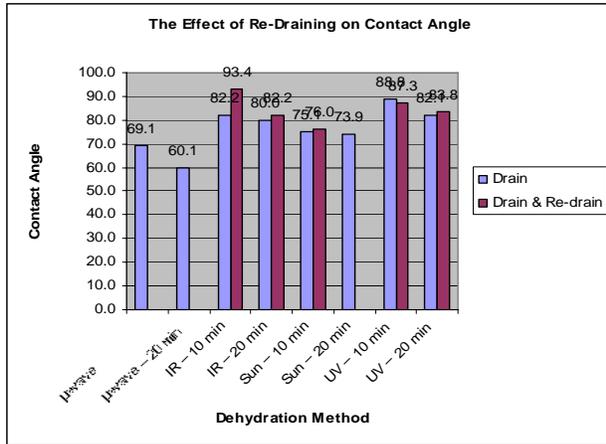


Figure 6. Contact Angles for Re-Drained Slides

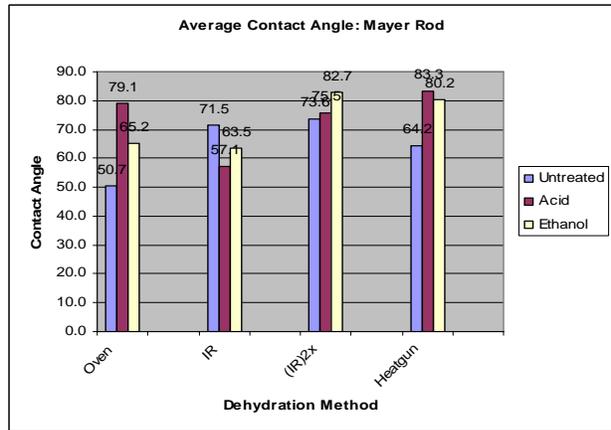


Figure 7. Effect of the Mayer Rod on Contact Angle

Mayer Rod

A new procedure was used for the next slides: the Mayer rod. After being coated by solution spray in combination with this rod, one was heated by the iron for 10 minutes and then analyzed while still hot. It revealed an average contact angle of 96.4°. This same slide, after cooling to room temperature, gave an average angle of 89.0°. Another slide was treated with solution and the rod and was then placed under the IR lamp for 10 minutes. It was then rinsed with water, and had contact angle of 91.5°. It was predicted that the hydrophobic quality of the slide would decrease after being rinsed with ethanol. When this prediction was tested, it was found that the prediction was correct because the slide showed an angle of 83.7° (Figure 7).

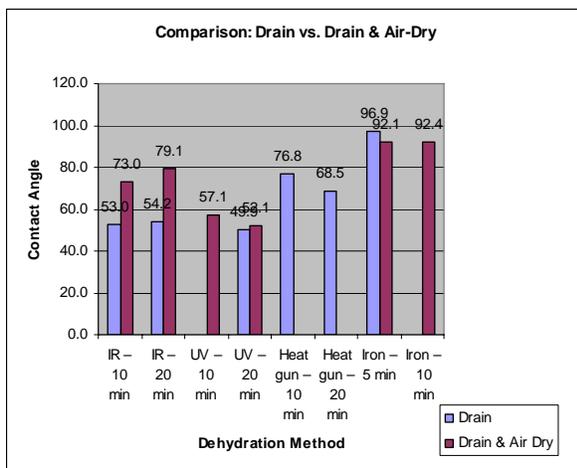


Figure 8. Comparison of the Effect of Draining vs. Draining & Air-Drying on Contact Angle

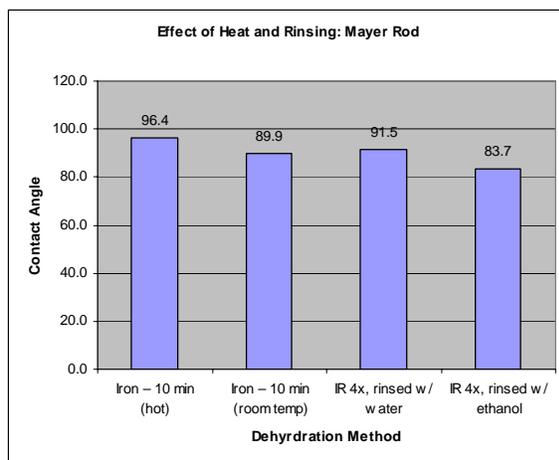


Figure 9. Average Contact Angle for Mayer Rod

Drain (15 min), Air-Dry (5 min)

The slides which were drained for 15 minutes showed that the draining method did not give very consistent results. It was hypothesized that this might be because the solution did not have enough time to form a bond with the low end of the slide before being heated. To test this, the slides were let to air-dry for 5 minutes after the 15 minute drain process. The slides which were air-dried and then received IR did significantly better when tested for contact angles. The UV-20 slides did slightly better when air-dried but average contact angle for 5 minutes of iron after air-drying was a few degrees lower than the average of slides which were not air dried. These results might have been more conclusive if every method that was originally used in the 15 minute drain slides was retested including the air drying step. Unfortunately, as can be seen in Figure 8, neither of the heat gun methods were repeated and no UV-10 min or Iron-10 min slides appear to have been tested in the first experiments.

Mayer Rod

These experiments were performed to compare untreated slides with slides treated with sulfuric acid and with slides treated with ethanol. In two of the four circumstances, the slides pre-treated with acid had high contact angles than untreated or ethanol-treated slides. Although the data is not very consistent, it does suggest that the acid pre-treat was effective. In addition, untreated slides had the lowest contact angles in all but one circumstance (Figure 9). The iron was not used as dehydration method for these slides.

Drop Method

For each dehydration method in this set of experiment, the slides were either left untreated, treated with sulfuric acid, treated with ethanol, or treated with acid followed by ethanol. They were all then coated with solution. Separate pipettes were used to drop the acid, ethanol, and solution onto the slides. For the slides that were in the oven for 48 hours, the ones which received acid and ethanol had the best contact angles (Figure 10). The acid and ethanol slides were also the best for slides that were put in the oven after each of two solution coatings. Surprisingly, the untreated slides had the highest average contact angles out of all of the slides that were placed under the IR lamp for 10 minutes once and twice. The pure ethanol treated slides also did well under these circumstances.

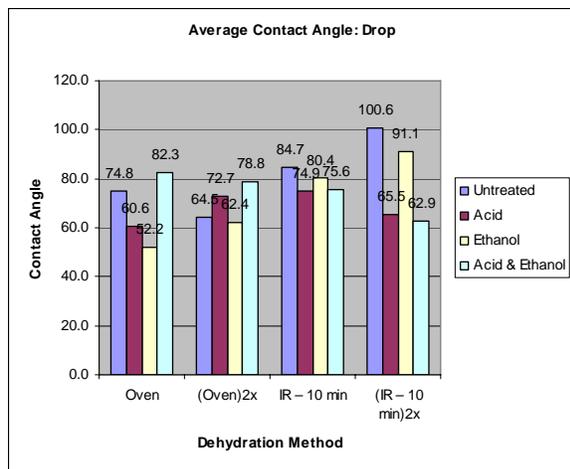


Figure 9. Average Contact Angle for Drop Method

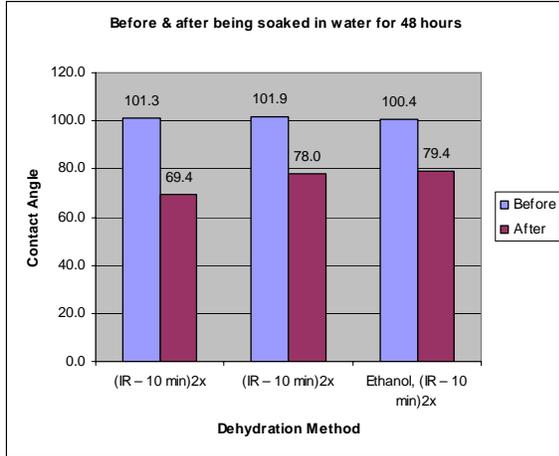


Figure 10 Effect of soaking for 48 hours

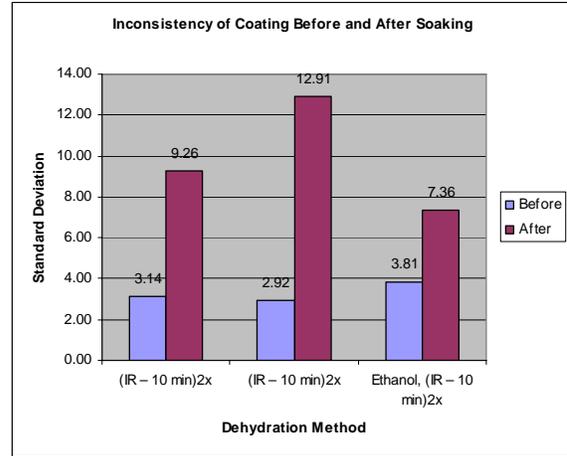


Figure 11 Inconsistency of results after soaking

After

Soaking in Water (48 hrs)

Three slides caught our attention because of their exceptional initial performance (Figure 12). The first was initially treated with two repetitions of the drop method and 10 minutes of IR radiation. The best initial contact angle was 103.5° and the mean of its angles were 101.3°. The second slide was an exact duplicate of the first, but its best angle was 104.8°, giving it a mean of 101.9°. The third was slightly different. It also received two repetitions of solution drop followed by 10 minutes of IR, but prior to these steps, we used a pipette to coat the slide with ethanol. Its best initial contact angle was 103.8° and the mean was 100.4°. After soaking for 48 hours in pure water, the performance of each slide dropped by 20° or more. The largest difference was for the first slide, whose mean plummeted from 101.3° to 69.4°.

DISCUSSION

Each procedure was performed on either one or two slides and four contact angles were measured for each slide. The contact angles were taken at different points lengthwise, evenly spaced. Thus, the standard deviation of the contact angles for a single slide is a measure of the completeness of the surface coverage of the technique. The actual application of the procedure should not have varied at different points across the individual slides because the physical bonding methods were applied to the whole slide in the exact same fashion, as with the spray and Mayer rod method.

To determine the variation of the data across multiple slides, the standard deviation of the slide means was determined. This is used to draw the significance of data from two slides prepared by the same specific procedure. This measure of variance can mainly be attributed to differences in the application of the procedure for both slides, a human error. But since there can also be natural variation in the technique and the actual slides may vary, no single cause can be concluded from this standard deviation. Instead, when this standard deviation of the means is very small, it can be inferred that human error in performing the procedure and natural variation of it are both minimal. When this variance is large, it can simply be concluded that the data

inconsistent, coming mainly from the properties of the procedure or the application of it. Conclusions from such data sets must be made with much caution, as human error may be a major contributor.

Covering the Surface with ODPA (Drop Method vs. Mayer Rod)

When comparing the drop method to the Mayer Rod method of physically bonding ODPA to the surface before washing with ethanol, results reveal that the drop method produced greater contact angles (Mayer Rod and Drop). This outcome is contrary to the original hypothesis that the Mayer rod would produce the most favorable results, but they do not tell the whole story. This data is deceptive because it was gathered before excess, non-bonded ODPA was washed away. After testing the contact angles of several slides with a surface coating applied by the drop method, they were soaked in water for 48 hours. At this point, their contact angles were about 25 degrees less and their standard deviations were three times as large (Drop: Before and After Being Soaked in Water for 48 Hours). This means that the initial hydrophobicity of the drop treated slides was from physical bonding of layers that came off in water. There was not much actual chemical bonding and it was not comprehensive. In reality, it was the Mayer rod that produced the greatest degree of chemical bonding.

This is attributed to the fact that the Drop Method does not in fact produce a monolayer. There were actually multiple layers, only one of which can eventually chemically bond. Before washing, each of these layers contributes to the measure of hydrophobicity. However, this excess ODPA is actually detrimental to the chemical bonding process. Due to the thickness of the ODPA covering, a reduced amount of energy actually interacted with the bottom layer, creating much less chemical bonding.

After soaking the Mayer rod slides with ethanol, not much ODPA was removed. The contact angles of the slides with 4 applications (where each application consists of an ODPA application step and a heating step) of the Mayer rod and heat procedure, each gave contact angles of around 90 degrees after ethanol washing step (Mayer Rod). Even with the washing, the contact angles from these slides were much better than the slides with two application of Mayer rod and no washing step (Mayer Rod). Thus, it can be concluded that replicate applications are important to improve effectiveness.

Covering the Surface with ODPA (Drain method)

For the Drain Method of physically bonding ODPA to the glass surface, only one slide was prepared for each procedure and four angles were measured for each slide. Immediately after the funnel was drained, the glass slides were removed and heated. Thus, the top of the slide standing in the funnel had the most time to evaporate the solution and bond to the ODPA because it was exposed to air the longest. The bottom of the slide was submerged in the ODPA solution until the very end of the draining and had little time to dry. The evaporative process is the critical step of physical bonding, so this meant that the bottom of the slide had minimal time to bond to the ODPA. In almost all of the slides using the drain method, a gradient and a large standard deviation was found in the contact angles (Drain). This was largely corrected for by allowing the slides to sit in the funnel for 5 minutes after draining had finished. The data reveals

that there was a significant increase in contact angles and a decrease in standard deviation when this step was added (Drain 15 min and Air Dry 5 min).

The Drain Method consistently had the greatest contact angles when it was drained for at least 45 minutes (Drain 45 min). A low draining time, 15 minutes, for the slides gave a very low contact angle, worse than any other physical bonding method tested (Drain 15). Nevertheless, 45 minutes is far less than the hours required for the T-BAG Method

Repetition

All of the various methods showed that performing a full procedure, physical and chemical bonding, on a slide multiple times produced a much more comprehensive coating with more chemical bonding (Spray and Drop and Drain 45 min) than one layer. For the multiple repetition experiments, procedures were performed only twice on some slides. The standard deviations decreased drastically and the contact angles increased with a repetition of the procedure. With a new coating applied by a physical bonding method, the ODPA Covered the surface more comprehensively. Based on the results, it is believed that up to four applications of a procedure will increase the chemical bonding and hydrophobic, although the contact angles will improve at smaller and smaller intervals. Different numbers of applications should be tested in future research. It was also found that heating the slides for 10 or 20 minutes under the IR lamp, UV lamp, or heat gun made no difference.

Sulfuric Acid Solution

Since sulfuric acid is a dehydration agent, it was expected that during heating, it would increase the amount of dehydration reactions between the oxide surface and the ODPA, and thus promote more chemical reactions in a shorter amount of time. Therefore, in one procedure, sulfuric acid was added to the ODPA solution in a small concentration as a catalyst before application to the surface. Note that this is a distinct experiment from the acid pre-treatment. In this case, the acid was part of the solution, not poured onto the glass prior to application of the solution. The acidified solution was added to the surface through the draining method. By comparing the contact angles from heating these slides with an iron to the draining method slides with a standard ODPA solution head by an iron, it was seen that the sulfuric acid actually lowered the contact angle (Sulfuric Acid in ODPA Solution). It is likely that the sulfuric acid interfered with the ODPA physically and chemically bonding to the surface by transferring a proton to the ODPA hydroxyl groups before the ODPA interacted with the surface.

Applying Energy for Dehydration Reaction

The data suggest that the type of energy did not greatly affect the bonding of ODPA to the slide. The IR, UV, and sunlight all produced slides with similar hydrophobic surfaces. The microwave, however, performed the worst, suggesting that these waves may have contained too little energy to encourage proton transfer.

What seems to be the determining factor in producing an effective hydrophobic surface is the medium of energy transfer. Looking at Table 2, [Drain 15 min], applying energy in the form

of electromagnetic radiation produced slides with contact angles between 40 and 60 degrees. With the heat gun, which uses air, the contact angles increased, ranging from 65 to 84 degrees, and with the iron, contact angles were consistently 96-97 degrees. The probable reasons for these differences are the concentration of energy applied and the distance from the slides. With the IR and UV energy, the lights held about six inches above the slides. Much of the energy could have escaped into the surrounding air and dissipated. The IR also did not have enough energy to force much chemical bonding. When slides heated by the IR were placed in water for 48 hours, their contact angles dropped around 25°, meaning that there was not much chemical bonding, just physical bonding that came off in the water (Drop: Before and After Being Soaked in Water for 48 Hours). With the heat gun, the energy was concentrated on the slides and it was held only a couple inches above them, with about 850° F of energy. The iron applied heat directly to the slide, which is likely the reason it was most effective, even more than the oven. It also could apply heat evenly and constantly, triggering the bonding of ODPa to the slides. Since our standard, the T-BAG method, had a contact angle of 95 degrees, the iron was just as efficient as this industry standard.

Pre-treatments

One factor that was tested is pre-treatments. There were two main pre-treatments that were experimented with: 5.4M sulfuric acid and ethanol. Very few slides treated with the sulfuric acid showed improvement in surface hydrophobicity. In majority of the cases, sulfuric acid tended to decrease the effectiveness of the ODPa treatment.

Sulfuric acid is a powerful reducing agent. Protons released from the ionized acid bind to the less reactive μ -oxo groups, transforming them into more reactive hydroxyl groups. Experiments show, however, that ODPa reacted less with the oxide surface after the acid pretreatment than before. It is very likely that the sulfuric acid treatment accomplished its intended purpose: to increase the number of hydroxyl groups on the oxide surface. It is more likely that the ODPa did not react to the entire surface, leaving regions covered with the ODPa monolayer and regions filled with hydrophilic hydroxyl groups, reducing the hydrophobicity of the surface.

It is important to note that the sulfuric acid was not washed off the surface after treatment. Phosphonic acids that had become reactive after becoming ionized could have lost that reactivity when it once again became protonated due to the presence of H^+ ions in the solution. The number of reactive ODPa reduces, and the amount of surface covered is reduced.

The data is inconclusive. We suggest that in future experiments the acid should be washed off before adding the ODPa solution in order to obtain more conclusive results. Ethanol pretreatment had no effect on the bonding of ODPa to the surface of the slide. Differences in contact angle between the ethanol pretreated slides and the standards were insignificant. Ethanol pretreatment was to clean the surface of any compounds that could prevent chemical bonding between ODPa and the surface.

Ethanol treatment may have been insignificant due to the fact that the ethanol was not wiped off after the surface after treatment. The ethanol did not wash away any of the compounds

but, rather, dissolved them in solution above the slide. Once the ethanol evaporated, the compounds redeposit onto the surface, once again interfering with ODPA bonding with the surface.

Computational Simulation

The octadecyl phosphonate and silicate VMD model faced several obstacles. Residues, basic structures that can be utilized to form a more complex molecule, had to be generated before the molecule could be observed as a whole. This meant that a new PDB file had to be made to display these new residues. The PDB files were constructed in another visualization program; MOE (Molecular Operating Environment). The intricate, technical language was hard to decipher and employ. However, once completed, the PDB files were displayed in VMD. Another issue the model confronted was out-of-plane bending (OOP Bending). Silicon is especially susceptible to OOP Bending because of its desire for multiple residue bonding sites. To avoid OOP Bending, the precise bonding angles of the residues and of the silicon were defined in VMD. The process of defining the bonding angles proved to be a very extensive process. Hence, the ODPA-silicon model could not be completed according to the afore-mentioned criteria within the allotted time period. With this technology it will hopefully be possible to discover more effective variations of ODPA.

CONCLUSION

Aside from the evaporative process used in T-BAG Method, the Drain Method for 45 minutes had the best contact angles, but large standard deviations within the same slide. The Mayer rod and the Drop Method had about the same mean contact angles, but the Mayer rod uses less ODPA solution than the Drop Method. In addition, the data suggested that multiple layers of ODPA added by the Mayer rod with heating in between onto the glass created a high contact angle. However, the data clearly indicates that the best method for heating the ODPA-covered slides was using iron; it was easily the most consistently comprehensive and was the only method to be as effective as the T-BAG standard, which had a contact angle of 95 degrees. The oven and the microwave did not produce high contact angles, and thus the surface was not covered completely with bonded ODPA.

Overall, it was difficult to draw conclusions from data collected because the sample size for each trial is too small. For the majority of the trials, the method was applied to only one or two slides. This was a problem because it was unknown whether variations in the contact angles within a slide and across slides were part of the natural variation inherent in the method itself or were rather a result from inconsistent control variables. For more definitive results, a larger sample size should be used in the future.

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APPENDIX A- DATA TABLES

ID	Description	Contact Angles (°)				Mean θ (slide)	Mean θ (group)	σ (slide)	σ (means)	σ (group)
		1	2	3	4					
Drain (45 min)										
HMU-10	Microwave – 10 min	65	72	72	68	69.1	-	3.2	-	-
HMU-20	Microwave – 20 min	67	64	67	42	60.1	-	12.3	-	-
HIR-10	IR – 10 min	101	82	72	74	82.2	-	13.1	-	-
HIR-10	Re-drain (15 min), IR – 10 min	90	92	92	101	93.4	-	4.9	-	-
HIR-20	IR – 20 min	88	88	77	67	80.0	-	10.0	-	-
HIR-20	Re-drain (15 min), IR – 20 min	83	80	81	85	82.2	-	2.3	-	-
HS-10	Sun – 10 min	89	72	71	68	75.1	-	9.2	-	-
HS-10	Re-drain (15 min), sun – 10 min	70	81	78	77	76.0	-	4.7	-	-
HS-20	Sun – 20 min	84	72	71	68	73.9	-	7.1	-	-
HS-20	Re-drain (15 min), sun – 20 min					-	-	-	-	-
HUV-10	UV – 10 min	100	88	81	87	88.8	-	8.2	-	-
HUV-10	Re-drain (15 min), UV – 10 min	88	101	73		87.3	-	14.2	-	-
HUV-20	UV – 20 min	101	88	65	75	82.1	-	15.8	-	-
HUV-20	Re-drain (15 min), UV – 20 min	76	87	83	89	83.8	-	5.6	-	-
Drain (15 min)										
XIR-10	IR – 10 min	54	54	56	48	53.0	-	3.7	-	-
XIR-20	IR – 20 min	50	58	54	55	54.2	-	3.6	-	-
XUV-20	UV – 20 min	53	52	43	51	49.9	-	4.7	-	-
XHG-10	Heat gun – 10 min	79	84	67		76.8	-	8.8	-	-
XHG-20	Heat gun – 20 min	76	65	65	68	68.5	-	5.4	-	-
XI-5	Iron – 5 min	97	96	97	97	96.9	-	0.5	-	-
0.01 M Sulfuric Acid in ODPa Solution, Drain (15 min)										
CSI-5	Iron – 5 min	88	88	82	70	81.7	87.1	8.7	7.6	8.7
CSI-5b		90	90	99	91	92.5		4.6		
CSI-10	Iron – 10 min	90	93	93	88	91.0	90.0	2.5	1.5	2.5
CSI-10b		86	90	89	91	88.9		2.3		
CSI-15	Iron – 15 min	89	84	83	76	83.0	85.1	5.1	3.0	5.5
CSI-15b		91	93	82	83	87.3		5.7		
Mayer Rod										
SRIR-10h	Iron – 10 min (hot)	97	97	96	96	96.4	-	0.5	-	-

SRIR-10r	Iron – 10 min (room temp)	90	92	93	84	89.9	-	4.0	-	-
SRW	IR 4x, rinsed w/water	90	91	92	93	91.5	-	1.0	-	-
SRE	IR 4x, rinsed w/ethanol	82	81	86	86	83.7	-	2.5	-	-
Drain (15 min), Air Dry (5 min)										
DTIR-10	IR – 10 min	62	72	81	77	73.0	-	8.2	-	-
DTIR-20	IR – 20 min	78	78	78	83	79.1	-	2.5	-	-
DTUV-10	UV – 10 min	64	55	48	62	57.1	-	7.3	-	-
DTUV-20	UV – 20 min	58	61	45	44	52.1	-	8.6	-	-
DTI-5	Iron – 5 min	88	92	94	95	92.1	-	3.3	-	-
DTI-10	Iron – 10 min	89	92	94	94	92.4	-	2.3	-	-
Mayer Rod; Untreated, Pre-Treated with 5.4 M Sulfuric Acid, or Pre-Wet with 100% Ethanol										
R1	Oven	50	51			50.7	50.7	0.6	-	0.6
R2						-		-		
R9	Ethanol, oven	51	46			48.8	65.2	3.4	19.4	15.6
R10		70	81	78		76.2		5.7		
AR1	Acid, oven	79				79.1	79.1	-	-	-
AR2						-		-		
R3	IR	58	59	65		60.5	71.5	4.0	15.6	13.3
R4		91	82	75		82.5		8.0		
R11	Ethanol, IR	53	62	56		57.2	63.5	4.6	11.0	10.0
R12		79	67			72.8		8.1		
AR3	Acid, IR	59	55	60		57.8	57.1	2.6	1.0	5.7
AR4		50	66	53		56.4		8.6		
R7	(IR)2x	45	70	71	63	62.2	73.6	12.2	18.8	16.7
R8		89	87	90		88.8		1.3		
R15	Ethanol, (IR)2x	79	74	82		78.4	82.7	4.4	6.1	5.8
R16		90	84	87		87.1		2.9		
AR7	Acid, (IR)2x	80	82	88	87	84.1	75.5	4.0	14.1	11.7
AR8		72	61	59		64.1		6.8		
R5	Heatgun	66	51	47		54.4	64.2	9.8	17.3	15.3
R6		82	76			79.0		4.7		
R13	Ethanol, heatgun	73	84	85		80.2	80.2	6.7	-	6.7
R14						-		-		
AR5	Acid, heatgun	77	85	91		84.5	83.3	6.9	2.1	5.2
AR6		82	81			81.5		0.8		
Drop; untreated, pre-treated with 5.4 M sulfuric acid, and/or pre-wet with 100% ethanol										
S14	Oven	73	66	86		74.8	74.8	9.8	0.0	8.7
S15		74	85	65		74.8		9.6		
A-S14	Acid, oven	45	50	49	56	50.0	60.6	4.4	17.4	13.9
A-S15		74	80	70		74.7		5.5		
S4	Ethanol, oven	50	44	50		47.7	52.2	3.6	6.4	8.7
S5		51	51	69		56.7		10.8		
A-S4	Acid, ethanol, oven	82	87	79		82.6	82.3	4.2	0.4	3.0
A-S5		84	83	80		82.1		2.1		

S19	(Oven)2x	63	52	65	67	61.6	64.5	6.6	4.1	5.9
S20		63	72	67	69	67.4		3.7		
A-S19	Acid, (oven)2x	67	85	69	69	72.3	72.7	8.2	0.5	8.9
A-S20		81	80	75	57	73.1		10.8		
S9	Ethanol, (oven)2x	87	82	52		73.4	62.4	19.1	15.6	18.6
S10		49	41	64		51.4		11.5		
A-S9	Acid, ethanol, (oven)2x	75	76	82	84	79.2	78.8	4.6	0.6	4.0
A-S10		80	74	82		78.3		4.0		
S11	IR – 10 min	98	79	93	100	92.4	84.7	9.5	9.1	15.7
S12		100	83	72		85.0		14.0		
S13		89	86	49		74.3		22.1		
A-S11	Acid, IR – 10 min	80	78	75		77.8	74.9	2.8	4.1	8.9
A-S12		84	59	73		72.0		12.8		
S1	Ethanol, IR – 10 min	84	70	56		69.9	80.4	14.3	9.5	13.5
S2		70	103	94		88.8		17.1		
S3		74	85	83	86	81.9		5.5		
ID	Description	Contact Angles (°)				Mean θ (slide)	Mean θ (group)	σ (slide)	σ (means)	σ (group)
		1	2	3	4					
A-S1	Acid, ethanol, IR – 10 min	59	61	65		61.4	75.6	3.1	20.1	15.8
A-S2		92	86	92		89.8		3.4		
S16	(IR – 10 min)2x	103	104	98		101.3	100.6	3.1	1.7	2.9
S17		99	104	105	100	101.9		2.9		
S18		96	102	98	99	98.8		2.2		
A-S16	Acid, (IR – 10 min)2x	53	80	62		64.9	65.5	13.4	0.7	11.1
A-S17		77	66	70	51	66.0		11.2		
S6	Ethanol, (IR – 10 min)2x	79	93	83		84.9	91.1	7.6	8.2	8.4
S7		101	104	96		100.4		3.8		
S8		86	87	90		87.9		2.1		
A-S6	Acid, ethanol, (IR – 10 min)2x	64	62	62	76	66.0	62.9	7.0	4.4	7.8
A-S7		64	56	51	69	59.8		8.1		
Drop; before and after being soaked in water for 48 hours										
S16	(IR – 10 min)2x, before	103	104	98		101.3	-	3.1	-	-
S16	(IR – 10 min)2x, after	63	64	83	68	69.4	-	9.3	-	-
S17	(IR – 10 min)2x, before	99	104	105	100	101.9	-	2.9	-	-
S17	(IR – 10 min)2x, after	76	79	94	63	78.0	-	12.9	-	-
S7	Ethanol, (IR – 10 min)2x, before	101	104	96		100.4	-	3.8	-	-
S7	Ethanol, (IR – 10 min)2x, after	69	84	86	79	79.4	-	7.4	-	-