Plasma Treated PET Films Grafted in Boronic Acid and Surface Properties

by

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Abstract:

Biofilm growth on medical equipment and bacterial infections following operations have previously been treated with antibiotics. Although that method has helped kill the majority of the bacteria, it leaves a strain of stronger, antibiotic-resistant ones that have adapted to survive and reproduce. Boronic acid contains a plethora of properties, such as determining the presence of glucose, detecting cancer in an early phase, and measuring dopamine levels more accurately in the brain. This research aims to explore another potential application of boronic acid because of its promising uses. Boronic acid is incorporated after the activation of surfaces with cool plasma. Plasma-activated surfaces polymerized in boronic acid can be applied to the biomedical and biotechnological domains as an antibacterial method to replace antibiotics on medical materials effectively. This will vastly improve the quality of medical equipment and sterilization within the medical and surgical fields.

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1. Introduction:

In recent years, the knowledge and use of plasma-treated surfaces have greatly expanded. Plasma can be used in a variety of ways with different gases, surfaces, intensities, and durations. In this experiment, polyethylene terephthalate (PET) films are treated with argon gas plasma in the Plasma Prep III device, produced by SPI Supplies, to create free radicals. The density and concentration of radicals can be altered by varying the time and power.

Plasma has helped create surfaces where biomolecules can be immobilized and act as ideal surroundings for cultures. Surfaces treated with plasma are not stable, and in the pursuit of that research, a hydrophilic surface environment is ideal for the growth of smooth muscle cells. Plasma processing on treated surfaces works well to immobilize proteins and encourage cell growth (Gupta *et al.* 2001). Because plasma-treated surfaces are considered unstable because of the free radicals, the reorganization that happens on the surface can be utilized in various ways, such as binding noble metal nanoparticles to plasma-treated polymers (Shen *et al.* 2017).

Shen's study took utilization of plasma on PET films in another direction. Strong interactions between nanoparticles of silver and the polymer help improve the antibacterial effectiveness of the surface (Shen *et al* 2017) and present new options for researchers to investigate, such as helping sanitize biomedical equipment within hospitals and other medical settings. Whereas previously contact killing was the main method of killing bacteria, the surface immobilization of silver nanoparticles shows promise. This method also uses plasma treatment to increase the amount of nanoparticles that adhere to the polymer surface (Shen *et al* 2017).

Furthermore, plasma can be used on PET films for antibacterial properties without the involvement of nanoparticles. The incorporation of acid into the grafting process of the PET films has forged the way for creation of new biomaterials. Already, polymers containing boronic acid have been utilized in helping treat HIV, diabetes, obesity, and cancer (Cambre & Sumerlin 2011).

The use of plasma is an effective alternate for antibacterials, especially for medical implants. Traditional antibiotics have resulted in stronger mutated strains of the bacteria, and bacterial colonies that have formed a biofilm are more resistant to antibiotics. Because antibiotics have short life spans and limited effectiveness, low-power plasma provides a new way to sterilize biomedical equipment (Traba & Liang 2015b). Results have shown that certain plasma conditions can cause the inactivation of biofilms and complete bacterial cell death. Excessive exposure to plasma can cause etching to occur on the surface, which is not ideal for the antibacterial testing of the surfaces (Traba & Liang 2015a).

Etching increases the surface area on a film such as the PET ones used. This, combined with the increased energy to which the film is exposed in the plasma device, creates increased adhesion on the surface (Deshmukh 2003). The ability of plasma to alter surfaces quickly makes it an attractive candidate for use within the health and production industry. This makes the development process more likely to be adapted on a mass scale to help improve the quality of medical equipment efficiently and effectively.

2. Materials and Methods:

2.1 Solutions and Surfaces

The two solutions initially created for the treatment of the PET films included one gram of boronic acid, *cis-1-propen-1-ylboronic acid*, dissolved in 50 mL of water and one in 50 mL of a half-ethanol/half-water solution.

Using tweezers, take the PET films from the stock of the ethanol and rinse in a conical of deionized water. Once dried, carefully using the tweezers, use a needle and thread to puncture the center of the films and string them for plasma treatment. No more than five films per piece of string should be used, because the films should not touch one another. In this experiment, three films were used with each solution.

2.2 Plasma Treatments

The Plasma Prep III is flushed it five times before testing the sample. Make sure the gas is turned on by opening the argon (Ar) gas tank cylinder.

Tape the PET film thread on the center backing and the upper midsection of the Pyrex inner chamber of the plasma device. Once the thread is secured, confirm that the films are not touching. The inner chamber can be inserted into the instrument with the open side facing inwards. Align the two dots found on the inner chamber with the circle that acts as the transmission electron microscopy (TEM) stage. Hold in the inner chamber while hitting the vacuum button; this step should last until the numbers appear. Wait for the chamber pressure to stabilize within the range of 360-370 millitorr. At this point, the radio frequency (RF) button is turned on and dialed up to 100 Watts and adjusted back to 80 Watts to calibrate it for the first trial. The second trial is conducted at 100 Watts, and both last for a duration of three minutes.

When three minutes have elapsed, turn the RF dial down to zero, and proceed to turn off the RF. Turn off the vacuum and vent the chamber until the internal pressure equals the external pressure. This should take less than five minutes and is indicated by the ability to remove the inner chamber once more. The inner chamber might be warm, so be careful when handling it.

After removing the inner chamber, carefully detach the tape from where it had secured the ends of the thread. Reattach the ends to an undisturbed corner of a fume hood without touching the treated films and allow 175 minutes for them to oxidize. The plasma device transfers energy from a source to the surrounding gas, causing the electrons to become energized and jump from the ground state into an excited state. This helps to form free radicals on the surfaces being treated. Allow the films to react with air for 75 minutes to form hydroperoxides and peroxides which will be used in the grafting process.

2.3 Grafting

The boronic acid solutions can be made while allowing the PET film to oxidize. Use tweezers to place the oxidized films in a glass bowl that contains the boronic acid solution (0.8002 g in 40mL of distilled water) that will be used. Place a watch glass over the labeled dishes and place on a tray in the oven. Close the oven door, making sure the seal is in place. Attach the vacuum hose and turn on the vacuum. Open the purge valve and then turn the right nozzle on the nitrogen (N) gas tank that finely adjusts the flow rate of the gas. Wait until the pressure gauge lies between twenty and fifteen psi, ideally fifteen, and then set a timer for five minutes. After five minutes, tighten the purge and allow the vacuum to increase the internal pressure until the gauge is close to 30 psi and set another timer for five minutes. Repeat the purging and vacuuming process two more times.

After the third time vacuuming, turn on the heat for the oven and purge once more for five minutes, vacuum for five minutes with heat, and purge for another five minutes with heat. The temperature should remain at approximately 80°C. The oven process should take 45 minutes total: 30 minutes for purging and vacuuming without heat and then 15 minutes with heat. Once the final purge is complete, turn off the vacuum, close the gas cylinder, and allow the PET films to sit overnight. Leave the vacuum tube connected, and the heat on at a constant temperature of 80°C.

3. Results and Discussion

3.1 IR of PET Films

The attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used in the range of 4000-400 cm^{-1} in the mode of percent transmittance. This instrument helps characterize the surface of the treated PET films to determine the chemical bonds present. There are two main regions: the fingerprint region from 400 cm^{-1} to 1500 cm^{-1}, and the diagnostic region which covers from 1500 cm^{-1} and on. The diagnostic region is where the clearest peaks and information about bonding can be determined.

In both diagrams (Figures 1 & 2), peaks in the diagnostic region appear at approximately 1700 cm^{-1} and within the 2800 – 3000 cm^{-1}. The one at 1700 cm^{-1} indicates the presence of a carbon double bonded to an oxygen in either an aldehyde, ketone, or carboxylic acid formation. The smaller double peak around the 2800 – 3000 cm^{-1} region shows that there is an alkane group (carbon bonded to hydrogen). At the 900 cm^{-1}, there is a peak for the boron from the bond between boron and carbon.

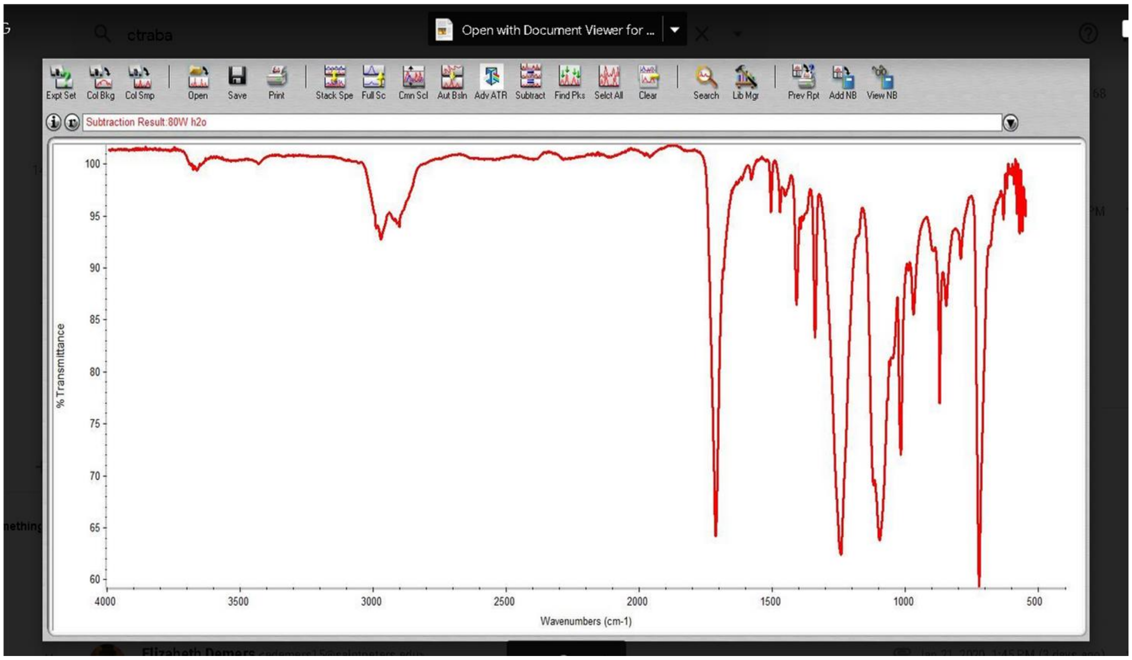
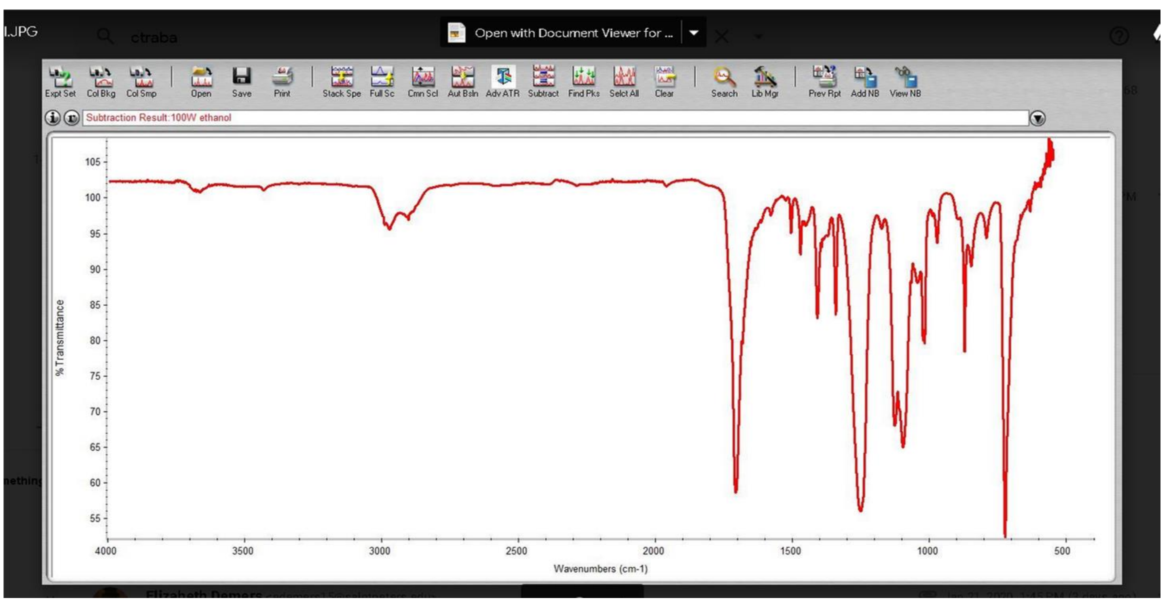


Figure 1. IR spectrum of the PET films treated at 80W in the plasma instrument and grafted in boronic acid



dissolved in water.

Figure 2. IR spectrum of the PET films treated at 100W in the plasma instrument and grafted in boronic acid dissolved in a 50/50 water and ethanol mixture.

3.2 Contact Angle of Treated and Untreated PET films

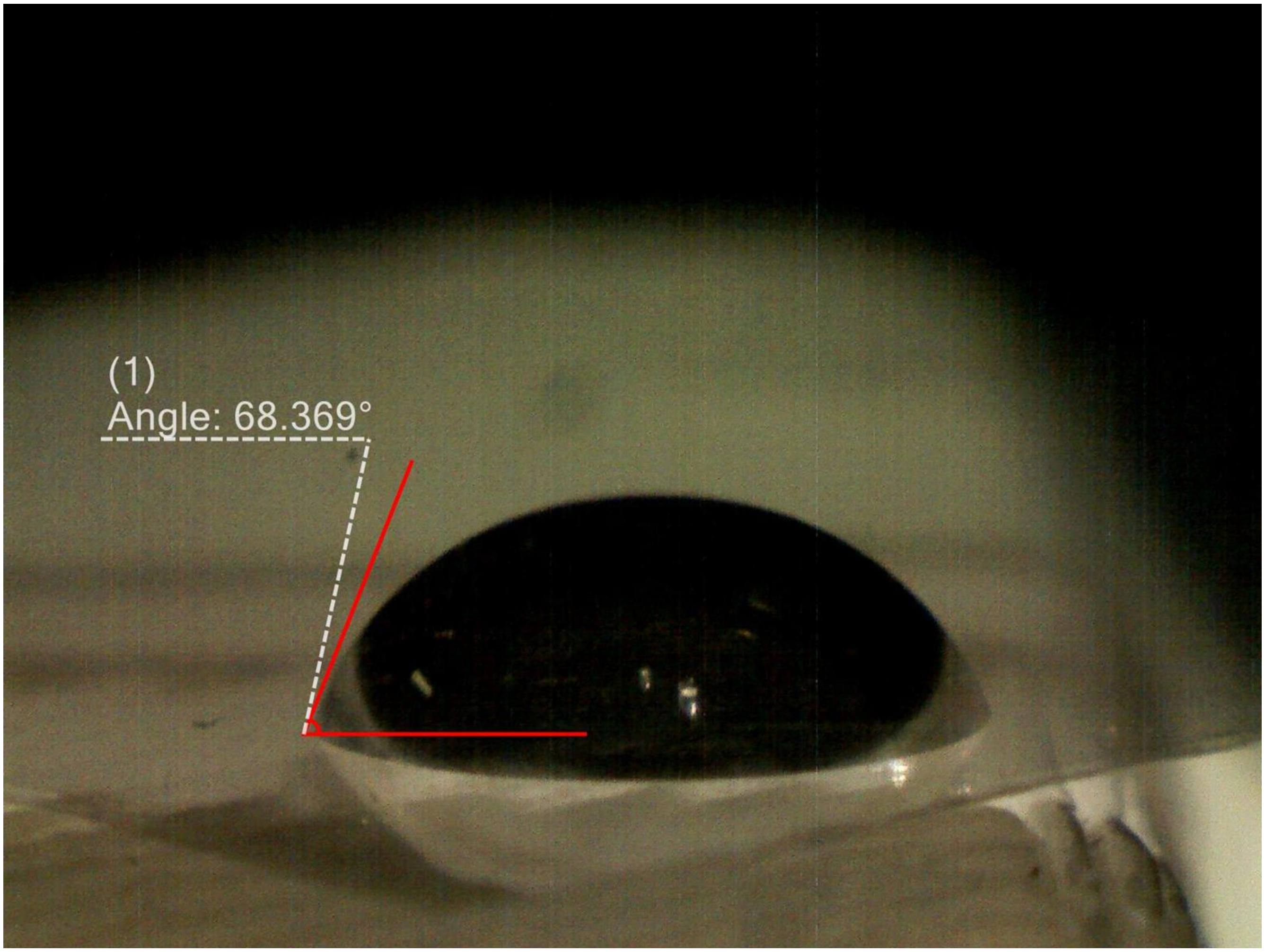


Figure 3. Untreated PET film as shown through the contact angle

As can be seen from the contact angle image, an untreated film has a water droplet upon it. The relationship is neither hydrophobic nor hydrophilic because the film has not been treated with plasma or boronic acid. The edges of the water droplet are not curled or over-extended as could be seen in a hydrophobic or hydrophilic relationship, respectively.

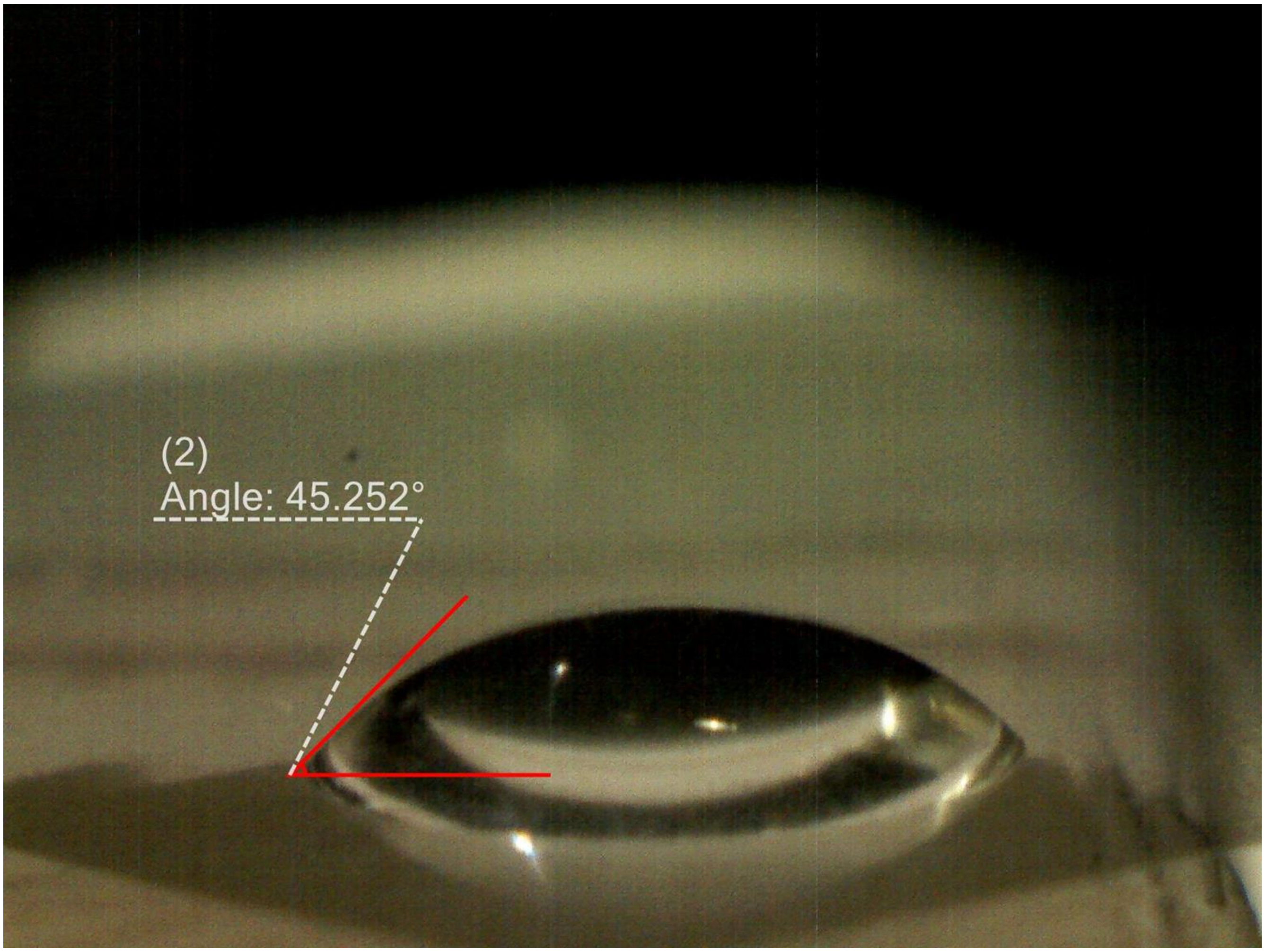


Figure 4. Treated PET film

Here the PET surface exhibits hydrophilic properties, because the water droplet is flatter, allowing an increased surface area of the water to interact with the surface. This occurs from free radicals that have formed following the plasma treatment. Empirically, this is shown through the more acute angle than that of the initially untreated film.

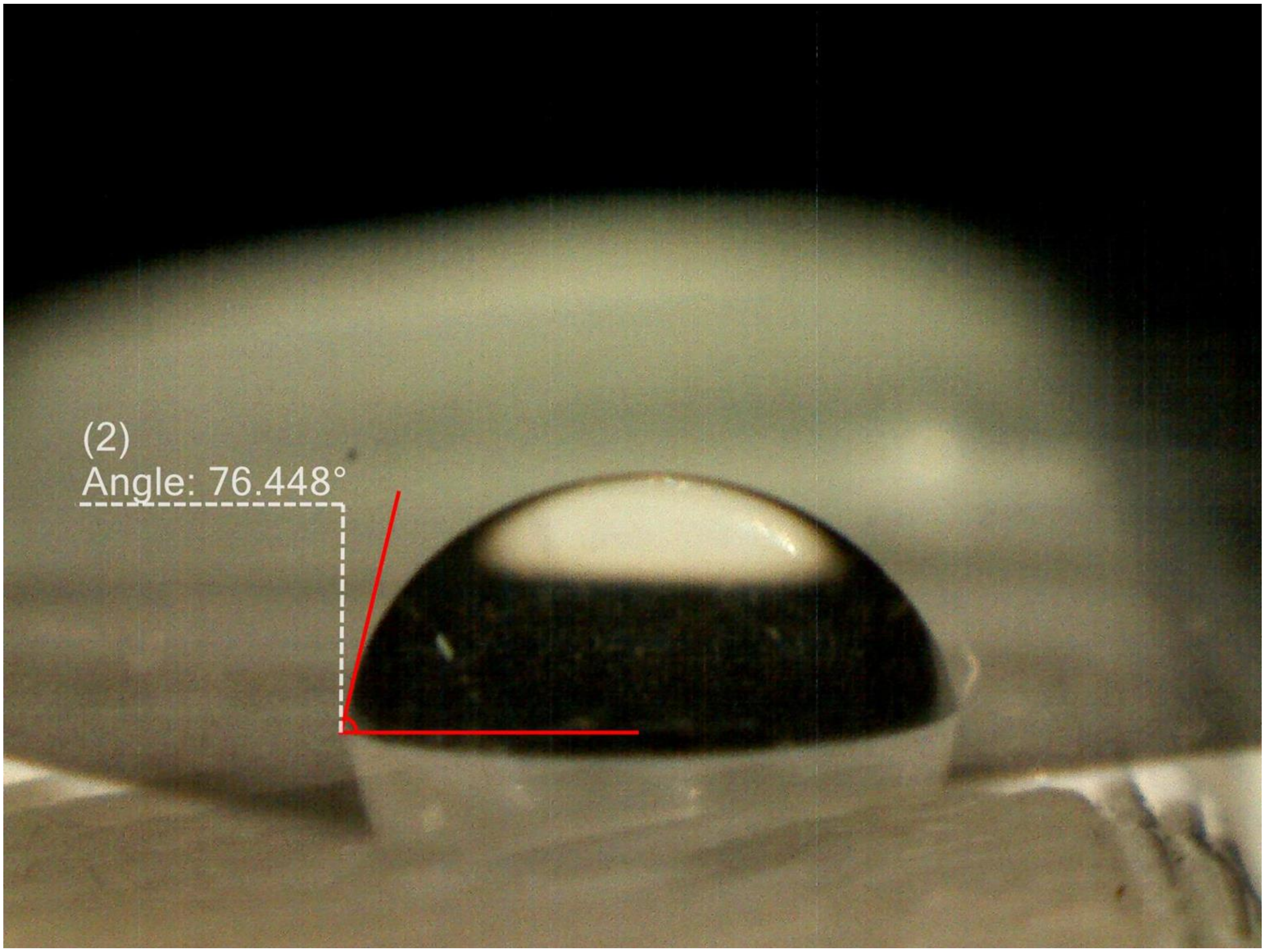


Figure 5. Plasma-treated PET film grafted with boronic acid

The plasma-treated PET film grafted with boronic acid is a hydrophobic surface. This is ideal for the experiment, because bacteria thrive in water. Because the surface rejects the water, this behavior will present itself rejecting bacterial growth. The angle depicted here is greater than both the untreated PET film control as well as the PET film that was treated, but not grafted, with boronic acid.

3.3 Discussion of Hydrophobic Surfaces

Hydrophobic properties exhibit an aversion to water. These can be found throughout nature, even in the phospholipid bilayer of the cell. By obtaining the hydrophobic results of a plasma-treated PET film grafted with boronic acid, possibilities of biomedical applications can begin to take form.

PET films were chosen because they are biocompatible. Hydrophobic surfaces discourage the presence of water and therefore bacterial growth, meaning that PET polymers can be potentially used for biomedical devices such as catheters.

4. Conclusion

Plasma-treated PET surfaces grafted in boronic acid are effectively hydrophobic and therefore discourage growth of bacteria and biofilms. Along with previously incapacitating biofilm growth through the use of plasma, these techniques can be used for development of treatments and products in hospitals. These anti-bacterial films are essential for advancing the sterilization standards of the medical and surgical fields. This innovative process has yet to be perfected; however, with further testing, the interaction between the surfaces and biological materials such as tissue cells or bacteria will be studied more thoroughly.

References:

Cambre, J, Sumerlin, B (2011) Biomedical applications of Boronic Acid Polymers, Polymer 52:21, 4631-4643

Deshmukh R, Bhat N (2003) The mechanism of adhesion and printability of plasma processed PET films, *Materials Research Innovation* 7:283-290

Gupta B, Plummer C, Bisson I, Frey P, Hilborn J (2001) Plasma-induced graft polymerization of acrylic acid onto poly(ethylene terephthalate) films: characterization and human smooth muscle cell growth on grafted films, *Biomaterials*, 23: 863-871

Parikh N, (2019) Anti-Biofilm Activity and Biocompatibility of Silver Nanoparticle Immobilized Biomaterials, *Honors Program, Saint Peter's University*.

Shen T, Liu Y, Zhu Y, Yang D, Sacher E (2017) Improved adhesion of Ag NPs to the polyethylene terephthalate surface via atmospheric plasma treatment and surface functionalization, *Applied Surface Science* 411:411-418

Traba C, Liang J (2015a) Bacteria Responsive Antibacterial Surfaces for Indwelling Device Infections, *J Control Release* 198: 18-25

Traba C, Liang J (2015b) The inactivation of *Staphylococcus aureus* biofilms using low-power argon plasma in a layer-by-layer approach, *Biofouling* 31(1): 39-48