Contact Angle Goniometer:

Hydrophobicity of Biomaterial Surfaces and Protein Coatings

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Abstract

The principles and applicability of surface structure and hydrophobicity of polymers (PS, PDMS), a ceramic (Glass), and a protein film are analyzed. The techniques of surface preparation and characterization are explained. Furthermore, the concept of surface free energy determination are discussed. The contact angle of these materials are determined using the ramé-hart Model 200 Standard Contact Angle Goniometer. In addition, the relationship between protein adsorption and hydrophilicity of the elastomer surfaces are explained by the conclusion that hydrophobic forces are not supported on surfaces with a contact angle θ <62.4°. Finally, the effect of surface morphology at it increase hydrophobicity using soot as a sample is observed.

I. Introduction

In order to restore or enhance the function of the original organs. Biomedical devices such as titanium hip implants, silicone finger joints, silicone heart valves, metallic stents, and vascular grafts are designed to interact with body tissue. Understanding of biomaterial surface interaction with water and proteins is essential for design of these biomedical devices.

In 1805, Thomas Young established a relationship between the surface energy and the contact angle. [1] He found that the interaction between the forces of cohesion and the forces of adhesion determines whether or not wetting, the spreading of a liquid over a surface, occurs. If complete wetting does not occur, then a bead of liquid will form, with a contact angle which is a function of the surface energies of the system. This relationship is expressed quantitatively as:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta \tag{1}$$

where θ is the contact angle, γ_{LG} is the liquid-gas surface tension, γ_{SL} is interfacial tension between solid and the liquid, and γ_{SG} is the surface energy of the substrate. When Surface free energy is minimized, droplets of liquid form and maintain on solid surfaces. Therefore, contact angle depends on balance between surface and interfacial energy, which provides a measure of liquid-solid surface interaction. [2]

When an implanted biomaterial comes into contact with biological fluids (e.g., blood) or tissues, which contains a huge amount of water, protein adsorption occurs immediately. It happens even before cells start growing at the surface. A physical property of material (or a molecule) that is critical to the interaction between the surfaces if these biomaterial devices and water is known as hydrophobicity; it classifies how these materials repel from a mass of water. H_2O s a polar molecule – it has a permanent electric dipole moment. Hydrophobic molecules

tend to be non-polar. Hydrophobic molecules in water often cluster together forming micelles. Water on hydrophobic surfaces will exhibit a high contact angle. [2] In the other hand, hydrophilic surfaces will exhibit a small contact angle. Superhydrophobic surfaces are those that are extremely difficult to wet; the contact angles of a water droplet exceeds 150° and the roll-off angle is less than 10°.[3] This is referred to as the Lotus effect, and is primarily a physical property related to interfacial tension, rather than a chemical property.

This experiment is intended to analyze the principles and applicability of surface structure and hydrophobicity of polymers (Polydimethylsiloxane, Polystyrene), a ceramic (Glass), and a protein film. The techniques of surface preparation and characterization are preformed, and the contact angle of these materials are determined. In addition, the relationship between protein adsorption and hydrophilicity of the elastomer surfaces are concluded. Finally, the effect of surface morphology in the effect of superhydrophobicity are observed.

Polydimethylsiloxane (PDMS) is a silicone elastomer. After polymerization and cross-linking, solid PDMS samples will present an external hydrophobic surface. Polystyrene (PS) is very chemically inert, being resistant to acids and bases but is easily dissolved many aromatic hydrocarbon solvents and one of the most widely used plastics. [4] Plasma oxidation can be used to alter the surface chemistry; it renders the PDMS, PS and Glass surfaces hydrophilic. Proteins are organic compounds made of amino acids arranged in a linear chain and folded into a globular or fibrous form. The amino acids in a polymer are joined together by the peptide bonds between the carboxyl and amino groups of adjacent amino acid residues. Interaction of proteins and water is governed by types of residues on protein surfaces. Serum albumin is the carrier of fatty acids in the blood. It is the most plentiful protein in blood plasma each protein molecule can carry seven fatty acid molecules.

II. Experimental procedure

The materials used in the experiment were PDMS, PS, and Glass. To determine the contact angle on each sample, the following steps were performed. Measurement results were recorded in degree.

A. SOP of Contact Angle Goniometer

The DROPImage program connected the ramé-hart Model 200 Standard Contact Angle Goniometer was used to determine the contact angle. The intensity knot on the illuminator and the stage height of goniometer were adjusted until the surface of your samples appeared on the screen. The micropipette was filled with DI water, then attached on the holder of the goniometer. Its position was adjusted so that the bottom portion of the needle was visible on the screen but above the sample. The pipette knot is rotated clockwise by was degree. As a result, a water droplet was forming at the bottom of the needle. While the water droplet remained at the bottom of the needle, the stage was slowly moved up to touch the droplet, which was then transferred onto the substrate surface. The green horizontal line on the screen was adjusted so it aligned to the substrate surface. The left and right vertical lines were adjusted so that the syringe needle was between the two vertical lines. The red horizontal line was adjusted so that it was between the bottom of syringe needle and the water droplet. After all things were properly set up, three contact angle measurements for each of the samples were made.

B. Surface cleaning

First, samples were cleaned with acetone and ethanol and then blown and dried. Next, oxygen plasma cleaning (**Harrick PDC-326**) was performed for 90 seconds to “burn” off surface hydrocarbons. It was taken into consideration the fact that that oxidized surfaces are stable for ~30 minutes in air, and after a certain time hydrophobic recovery of the surface is inevitable

independently of the surrounding medium whether it is vacuum, air, or water. [2] Contact angle measurements were performed on all samples.

C. Surface modification using BSA protein exposure

The three petri dishes are prepared and labeled as PDMS, PS and glass. Using pipet the dishes were filled with 4ml of phosphate buffer saline solutions containing bovine serum albumin. The samples were completely submerged in the solution for 10 minutes. The contact angle measurement was made on all samples.

D. Deposition of superhydrophobic coatings

Using a wax candle, a glass slide was exposed to the candle flame. The flame was pressed with a glass slide to reduce the burn efficiency in order to increase soot production. Double sided Scotch tape was attached to another class slide, and soot was transferred to the sticky Scotch tape. Then, the contact angle measurement was performed.

III. Results

Using the DROPImage program, the contact angle measurements of PDMS, PS and Glass were determined after prolong storage in ambient atmosphere and after surface cleaning using oxygen plasma. The contact angle measurement of soot generated using a wax candle was also performed and recorded.

As shown in Table 1, the mean of the contact angle measurements of PDMS after prolong storage in ambient atmosphere was found to range from 61.4◦ to 92.0◦ whereas the mean of the contact angle measurements of PDMS after surface cleaning was found to was found to decrease showing a range from 0.0◦ to 13.4◦. The mean of contact angle measurements of PDMS after the sample was submerged in buffer saline solutions containing bovine serum albumin for 10 minutes were found to be range from 15.1◦ to 62.1◦.

Table 1: The contact angle measurements of PDMS after prolong storage in ambient atmosphere, after surface cleaning using oxygen plasma and after surface modification using BSA protein exposure.

prolong Storage in Ambient Atmosphere			Surface Cleaning Using Oxygen Plasma			Surface Modification Using BSA Protein Exposure		
Angle 1	Angle 2	Mean	Angle 1	Angle 2	Mean	Angle 1	Angle 2	Mean
61.6◦	61.2◦	61.4◦	6.9◦	13.0◦	10.0◦	60.2◦	63.9◦	62.1◦
69.3◦	69.8◦	69.6◦	0.0◦	0.0◦	0.0◦	20.2◦	10.0◦	15.1◦
91.2◦	92.6◦	92.0◦	15.7◦	11.1◦	13.4◦	37.5◦	34.5◦	36.0◦

For the PS sample, the mean of the contact angle measurements after prolong storage in ambient atmosphere was found to range from 89.3◦ to 90.0◦ whereas the mean of the contact angle measurements after surface cleaning was found to decrease showing a range from 20.0◦ to 13.8◦, as indicated in Table 2. The contact angle measurements of PS after it was submerged in buffer saline solutions containing bovine serum albumin for 10 minutes were found to be all 0.0◦.

Table 2: The contact angle measurements of PS after prolong storage in ambient atmosphere, after surface cleaning using oxygen plasma and after surface modification using BSA protein exposure.

prolong Storage in Ambient Atmosphere			Surface Cleaning Using Oxygen Plasma			Surface Modification Using BSA Protein Exposure		
Angle 1	Angle 2	Mean	Angle 1	Angle 2	Mean	Angle 1	Angle 2	Mean
89.6◦	89.0◦	89.3◦	13.7◦	13.9◦	13.8◦	0.0◦	0.0◦	0.0◦
84.7◦	84.8◦	84.8◦	19.1◦	21.0◦	20.0◦	0.0◦	0.0◦	0.0◦
89.7◦	90.3◦	90.0◦	14.0◦	14.7◦	14.4◦	0.0◦	0.0◦	0.0◦

For the Glass sample, the mean of the contact angle measurements after prolong storage in ambient atmosphere was found to range from 34.5◦ to 31.2◦ whereas the mean of the contact angle measurements after surface cleaning was found to decrease showing a range from 20.0◦ to 13.8◦, as indicated in Table 2. The contact angle measurements of PS after it was submerged in buffer saline solutions containing bovine serum albumin for 10 minutes were found to be all 0.0◦.

Table 3: The contact angle measurements of Glass after prolong storage in ambient atmosphere, after surface cleaning using oxygen plasma and after surface modification using BSA protein exposure.

prolong Storage in Ambient Atmosphere			Surface Cleaning Using Oxygen Plasma			Surface Modification Using BSA Protein Exposure		
Angle 1	Angle 2	Mean	Angle 1	Angle 2	Mean	Angle 1	Angle 2	Mean
29.3◦	33.0◦	31.2◦	0.0◦	0.0◦	0.0◦	0.0◦	0.0◦	0.0◦
32.4◦	31.4◦	31.4◦	0.0◦	6.0◦	3.0◦	0.0◦	0.0◦	0.0◦
34.7◦	34.2◦	34.5◦	9.3◦	0.0◦	4.65◦	0.0◦	0.0◦	0.0◦

In comparison of the contact angle measurements between the three samples (PDMS, PS and Glass) after prolong storage in ambient atmosphere, the measurements of the PS sample were found to be the largest while the measurements of the PS sample were found to be the smallest. Good agreement was observed among the three samples in term of the change in the contact angle measurements after surface cleaning and modification; all of the sample measurements were found to decrease. However, a difference in contact angle between BSA-treated surfaces of the different samples were found; measurements for both PS and Glass samples were all found to be 0.0◦ whereas measurements for PDMS sample were found to range 15.1◦ to 62.1◦.

Table 4 shows the contact angle measurements of Soot; they were found to range from 66.4◦ to 138.1◦, indicating the largest contact angle of all materials used in the experiment.

Table 4: The contact angle measurements of Soot

Angle 1	Angle 2	Mean
134.2◦	136.4◦	135.3◦
137.2◦	139.1◦	138.1◦
64.4◦	68.3◦	66.4◦

IV. Discussion

The air exposure clearly impacts how the surfaces interact with water. As shown in Table 1, 2 and 3, all of the materials (PDMS, PS, and Glass) experience a notable reduction in the contact angle after surface cleaning using oxygen plasma in compare to their native state (prolong exposure to ambient atmosphere). This clearly indicates that air exposure modifies the surfaces to be more hydrophobic. This phenomena can be explained by the fact that the water molecule forms an angle, with hydrogen atoms at the tips and oxygen at the vertex. Since oxygen has a higher electronegativity than hydrogen, the side of the molecule with the oxygen atom has a partial negative charge. The dipole-dipole interaction produce attractive force between water molecules other polar molecules. [2] These results agree with the literature. [1,3,5] After surface cleaning, the oxidized surface resists adsorption of hydrophobic and negatively charged species and become more hydrophilic.

Water is expected to interact the surface of materials based on their known structure. The chemical formula for PDMS is $CH_3[Si(CH_3)_2O]_n Si(CH_3)_3$. PDMS is non polar, and is inherently hydrophobic. This surface chemistry makes it difficult for polar solvents (such as water) to wet the PDMS surface, and may lead to adsorption of hydrophobic species. PS is long chain hydrocarbon wherein alternating carbon centers are attached to phenyl groups with a chemical formula of (C8H8)n; it contains the chemical elements carbon and hydrogen. PS is also nonpolar and expected its surface to show a minimum interaction with water. [4] Glass is largely made out of a giant covalent structure of SiO2 molecules - each silicon atom is bonded to two oxygens. The large difference in electronegativity between the constituent atoms in this structure makes the bonds strongly polar. As such, the electron-rich oxygen is capable of attracting electron-deficient hydrogens in H2O molecules. [5]

A difference in contact angle between BSA-treated surfaces of PDMS, PS and Glass is observed. The data suggest that protein treatment in PDMS is not as effective as in PS and Glass. Adsorption of proteins on surfaces depends on protein-biomaterial surface groups. The value of water wettability might then be viewed as a criterion for distinguishing a surface as either "protein adherent" or "protein non-adherent". [3] Studies have suggested a water contact angle limit of 65° for the observation of long range hydrophobic attractive forces on surfaces. Yoon et al. who measured the hydrophobic (attractive) and hydrophilic (repulsive) forces on different wettable silica surfaces using AFM and suggested that hydrophobic forces were not supported on surfaces with θ <62.4°. [6]

The superhydrophobic contact angle measurements using soot as a sample were found large. It is due to the fact that if the surface is structured into an array of such bumps, the resultant effect is an increased contact angle observed macroscopically. However, the superhydrophobic contact angle measurements did not exceed 150 or be 180 degrees because the sample was not prepared in a nm scale. [2] That leaded to the existence of spaces between the carbon atoms and variations in the contact angle on each spot.

V. Conclusions

The principles and applicability of surface structure and hydrophobicity of polymers (PS, PDMS), a ceramic (Glass), and a protein film are analyzed, the techniques of surface preparation and characterization are explained. Furthermore, the concept of surface free energy determination are discussed. The contact angle of these materials are determined using the ramé-hart Model 200 Standard Contact Angle Goniometer. In addition, the relationship between

protein adsorption and hydrophilicity of the elastomer surfaces are concluded. The effect of surface morphology in the effect of superhydrophobicity was observed.

The experiment succeeded in showing that prolong Storage in ambient atmosphere modifies the surfaces of to be more hydrophobic while surface cleaning using oxygen plasma modifies them to be more hydrophilic. It was asserted that protein adsorption on different surfaces varies based on the contact angle with a limit of 65 degrees. It was also concluded that in order to achieve superhydrophobic angle, samples should be prepared in nm scale. Some limitations exist in the experiment. There were some variations in the angle measurements of PDMS. It could be due to the fact that the sample was not dry enough. Improvements can be made in the experiment by letting the samples suppressed in the protein solution and dried for a longer time. Also, producing a soot sample with a nanometer scale will result in a more accurate contact angle measurements.

References

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