Oil-Water Separation Efficiency of Carbon Nanotubes in 3D-Printed Polymer Matrix

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Honors Research in Nanotechnology

ABSTRACT: Oil pollution is becoming a worldwide issue that has the potential to negatively affect marine life and ecosystems. Toxic oil contaminants, including crude oil, diesel oil, and gasoline, pose a threat to many marine organisms and even humans. To address this issue of oil pollution, methods such as bioremediation, the use of oil dispersants, and in situ burning have been tested, although these treatments are often limited in scale and may have negative secondary effects.

This research aims to create a method of separating oil and water using hydrophobic carbon nanotube (CNT) membranes with polydimethylsiloxane (PDMS) bases, which are reusable and could be produced on a larger scale using a simple process. The CNTs were made through chemical vapor deposition, then sonicated with the PDMS base to homogenize the mixture, which can then be printed out using a 3D printing extruder into a mesh of any shape or size. Several membranes containing different wt% of CNTs were tested using water angle contact test to determine their hydrophobicity. The positive results of these tests show that CNT membranes with PDMS bases present a potential alternative method for reducing oil pollution through the separation of oil and water droplets - however, further study is needed to enhance their efficiency.

INTRODUCTION

Oil pollution has become a worldwide issue due to the increase in oily wastewater produced by industrial processing of petrochemicals, metals, and food, in addition to frequent oil spills.[1] The oil wastes that are released into the ocean can cause severe marine pollution that degrades the health of marine organisms, animals that come in contact with the oil, and humans if contaminated marine organisms are consumed.[2] Some common types of oil that appear in the waters include crude oil, diesel oil, and gasoline.[3] Each type of oil possesses different harmful effects to the environment. Crude oil, for example, contains toxic hydrocarbons that can be dispersed throughout the ocean in the form of droplets and reach the sea bottom. Oil droplets on the seafloor are long-lasting and can harm bottom plants and animals. If ingested by fish and other sea animals, the hydrocarbons will become part of their flesh and fat, which are isolated from the natural degradation process.[4]

To solve the issue of oil pollution, numerous methods have been developed to clean and separate waste oils from water. Some methods include bioremediation, oil dispersants, and in situ burning. Bioremediation is the use of microorganisms or microbial methods to degrade contaminants, specifically oil pollutants. It is inexpensive and can eliminate wastes permanently, but are limited to some chemicals that are not amenable to biodegradation. Some microbial contaminants can also produce toxic metabolites that will further harm the environment.[5] Oil dispersants are used to break apart oil suspended in water and turn them into smaller droplets for the biodegradation of naturally occurring bacteria. Although this method is beneficial for its ability to be implemented in large surface areas via airplanes, it is a concern that the dispersants themselves may also be toxic, even more so than the oil. Lastly, in situ burning is when oil is ignited on water and burned in large portions to keep oil away from the shoreline. This method can be critically affected by the weather and can shift the negative environmental impact from the ocean to the air.[6] Many cleaning methods, similar to the ones mentioned above, have potential environmental risks that can do more harm than good to the ocean. With the rise of popularity in nanotechnology, there has been increased studies that use nanomaterials to target oil-water separation.

Studies have shown that the applications of certain nanomaterials can be used for environmental decontamination. As shown in the figure below, there are numerous ways to clean up oil using nanomaterials. For instance, a study conducted by Rice and Penn State University discovered that boron-doping nanotubes can turn them into spongy reusable blocks that can absorb oil spilled in water.[7] Another study used commercially available polyurethane foams functionalized with colloidal superparamagnetic iron oxide nanoparticles that can efficiently separate oil from water.[8]

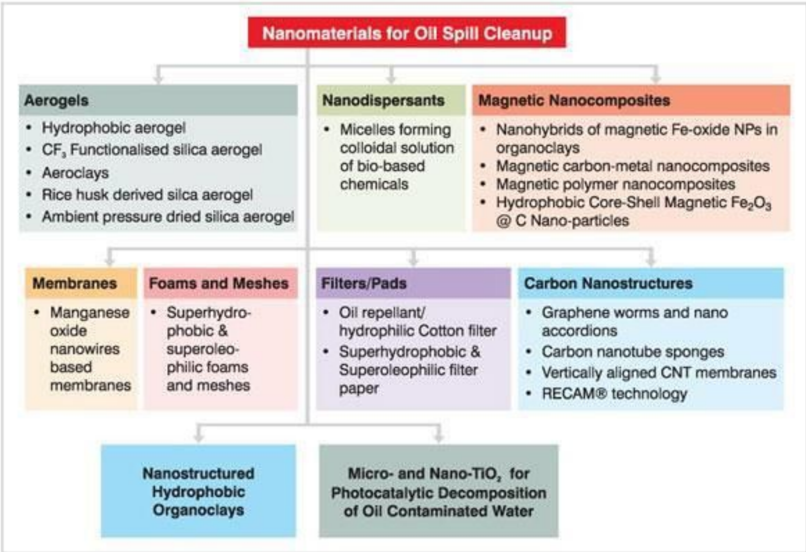

Figure 1. Examples of nanomaterials for oil spill cleanup.[9]

However, many of these fabrication and synthesis methods involve complicated handlings which can lead to weak mechanical stability and oil-water separation efficiency. In recent years, more studies have been done on using superhydrophobic porous membranes, which repels water but allows oil to pass through. Different methods exist to create these membranes such as spray-coating and solution-immersing, although these methods can often clog pores and create inhomogeneous membrane pores, thus losing their hydrophobic property.[10] This paper is inspired by a study that 3D printed a superhydrophobic membrane with viscoelastic ink of polydimethylsiloxane (PDMS) and nanosilica particles for oil-water separation. 3D printing the membrane allows the membrane pores to be homogenous and well-structured while maintaining its superhydrophobicity.

There are reports that show carbon nanotubes, tube shaped material made out of carbon that have diameters ranging on the nanoscale, can be used to separate emulsified oil and water mixtures with higher efficiencies than commercial filtration membranes.[11] CNTs composite membranes can also improve water treatment with their electrochemical function with membrane separation processes.[12] Knowing that carbon nanotubes are highly porous, low in density, and have hydrophobic properties, the aim is to create a simple method to make an effective and efficient superhydrophobic CNT-filled PDMS membrane for oil-water separation. The efficiency between nanosillica filled membranes and CNT filled membranes should be compared and evaluated.

METHODS

Part 1. Carbon Nanotube Synthesis

To synthesize aligned CNTs, chemical vapor deposition (CVD) was used. The precursor solution, 0.625 g of ferrocene and 25 mL of toluene, were mixed together in a beaker. The solution was then loaded into a syringe at the end of the CVD chamber. The temperature of the chamber was set at 200°C on the injection end and 850°C at the reaction end. Once the temperatures were reached, the flow meter for the injection of the precursor was set at 12 milliliters per hour. The carrier gas of 95% argon and 5% hydrogen were used to initiate the flow rate. The reaction continued for 2 hours until the syringe was completely empty, and the CNTs were allowed to cool before being collected. The cooling process inside the quartz tube ensures the purity of the CNTs.[13] When the quartz tube has been completely cooled, the CNTs were collected by a silicone spatula.

To confirm the presence of CNTs in the desired shape, the sample was observed under the scanning electron microscope (SEM). In figure 2, nanofibers can be seen, confirming that the tubes were successfully made. However, it cannot confirm whether the nanotubes were aligned or not.

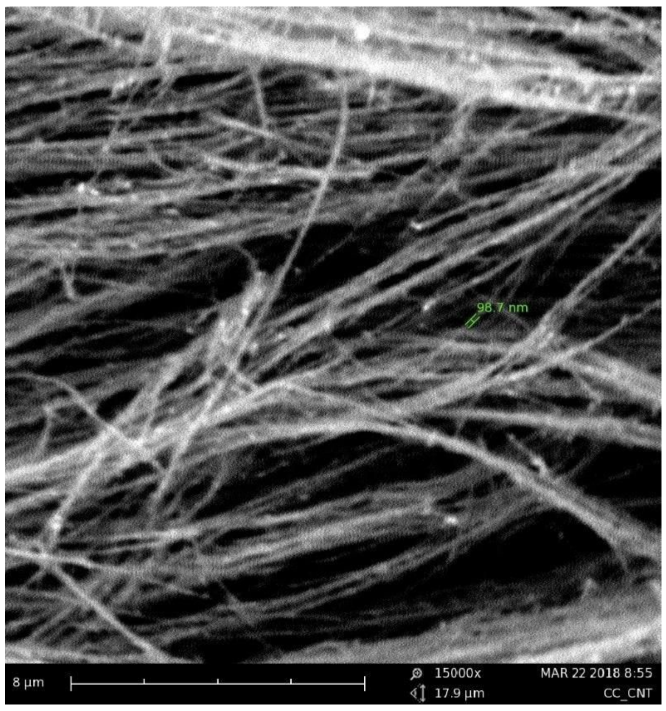

Figure 2. SEM image of CNT sample showing nanotubes used in experiments

Part 2. CNT/PDMS Ink Base

The ink base was prepared by first mixing 0.655g of CNTs (6wt%) with 0.888 g of the curing agent (methylhydrosiloxane with Pt catalyst, Part B, Dow Corning) into a petri dish. After mixing the CNTs with part B using a spatula, 0.078 g of the inhibitor 3-butyn-1-ol (purchased from Sigma-Aldrich Company) was added in. Lastly, 8.8 grams of polydimethylsiloxane (PDMS) (sylgard184, Part A, Dow Corning) was added into the petri dish using a pipette. Once the mixture with the CNTs is evenly distributed, the petri dish was sealed with parafilm and then vortexed for 80 minutes at 650 rpm. After the mechanical agitation, the CNT/PDMS mixture was transferred into a syringe tube and dispensed out in the shape of a mesh around 4 cm long and 3 cm wide with pores that are less than 0.5 cm wide. The CNT/PDMS mixture was dispensed onto a Teflon board then thermally cured at 120 °C for 1 hour.

Part 3. CNT Sonication/Ball Mill for Homogenized Texture

After a few initial trials, when the CNTs were mixed directly for the ink, the texture of the ink was too rough and uneven, with small clumps of CNTs dispersed throughout. Therefore, the texture of the CNTs had to be homogenized before mixing with the other parts. The method used was to put CNTs inside an ultrasonic bath sonicator. The sonicator is able to homogenize the texture of the CNTs to a certain extent, making the particles much finer. Ethanol was used to disperse the CNTs, and because it is evaporated afterwards it does not alter the characteristics of the carbon nanotubes.

CNTs were added into a 15mL centrifuge tube with ethanol that submerged the CNTs completely. The second method used was adding CNTs into a Retsch ball mill for 10 minutes at 300 rpm with 2 minute interval rotational changes.

Part 4. Water Contact Angle (WCA)

One way to measure the hydrophobic properties of the mesh is to measure its water contact angle. A light source was placed behind a flat surface where the mesh is placed. Different volumes of droplet were placed on the flat side of the mesh (5,10,30 microliters) and the angle that the water created with the mesh was analyzed in ImageJ. If the angle is greater than 90, then the surface is considered hydrophobic; when it is less than 90, it is considered hydrophilic. In this study, a hydrophobic surface is desired for separating oil and water.

Part 5. 3D Printer Extruder

To make the universal paste extruder, the printer extruder body and the other parts are 3D printed with files obtained from thingiverse.[14] The instructions to assemble the extruder can be found here. After the extruder was assembled, it was swapped with the lulzbot Taz 6 printer extruder. The ink base is loaded into a 10mL syringe and secured onto the extruder.

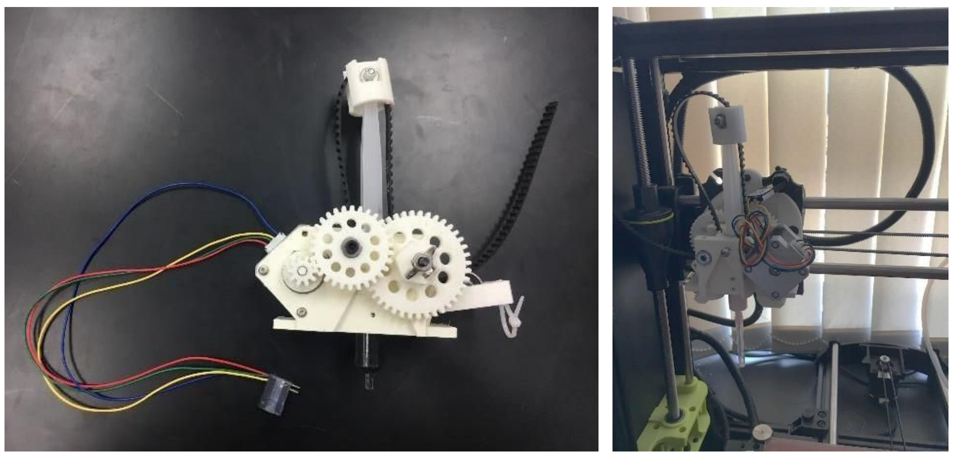

Figure 3 (left) Printed Universal Paste Extruder. **Figure 4 (right)** Printed Extruder on Printer.

DATA AND ANALYSIS

Hydrophilic or Hydrophobic

To test for the hydrophobic characteristic of CNTs in the mesh, water, sunflower oil, and hexane were used in this experiment. The mesh was placed on top to cover the opening of a flask. Water, sunflower oil, and hexane were then dropped separately onto the mesh using a pipette. Between each solution, the mesh must be wiped dry before proceeding to prevent mixing up the solutions. The second test involved with mixing hexane with dyed water and sunflower oil with dyed water. When running the test, the dyed water should remain on top of the mesh, whereas the hexane and the oil should pass through the mesh since they are all non-polar.

Figure 5, 6. Water suspended on 7 wt% CNT-PDMS mesh. Multiple water droplets cover the pores in the mesh, however, they do not pass through the pores

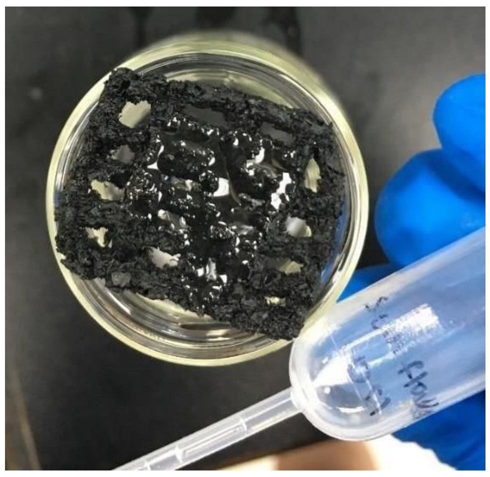

Figure 7. Complete flow through of sunflower oil through the 6 wt% CNT-PDMS mesh

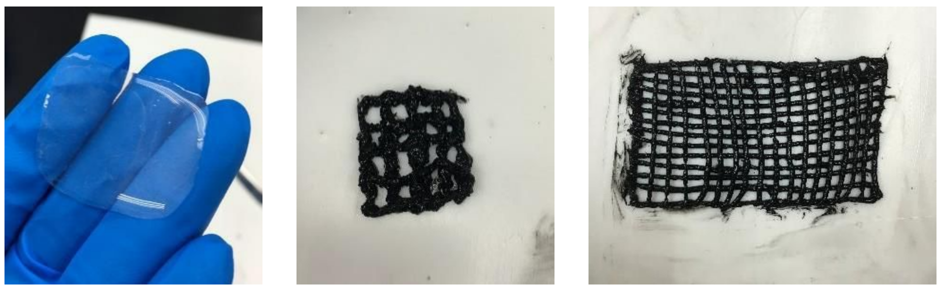

Figure 8 (left). Negative Control. **Figure 9 (center).** 3 wt% CNT-PDMS mesh. **Figure 10 (right).** 1 wt% CNT-PDMS mesh

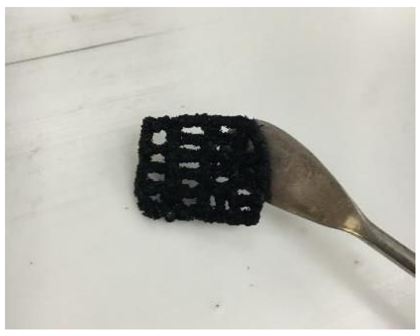

Figure 11. wt % CNT-PDMS mesh after thermal curing.

Water Contact Angle Results

The angle that the water droplet creates with the mesh was measured and summarized in the table below.

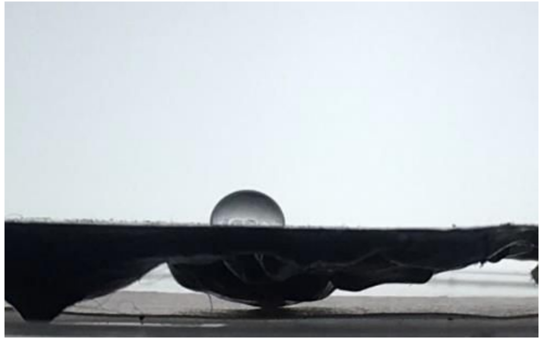

Figure 12. A 10 µL droplet on 1 wt% mesh.

CNT Weight Percent/Angle (°)	5 µL	10 µL	30 µL
0 wt%	107.08	93.23	100.52
1 wt%	110.2	97.19	87.82
3 wt%	94.45	103.39	106.1
6 wt%	114.03	112.48	120.94

Table 1. Water contact angles for different CNT wt% and volume of water.

A higher CNT wt% generally resulted in a greater WCA. As seen in figure 14, there is a positive correlation between the amount of CNTs with the angle that the water creates. Both mesh with 3wt% and 6wt% CNT showed a higher WCA compared to the other wt%. However, more data is required for the different amounts of wt% in order to confirm the relationship between the amount of CNTs and the WCA.

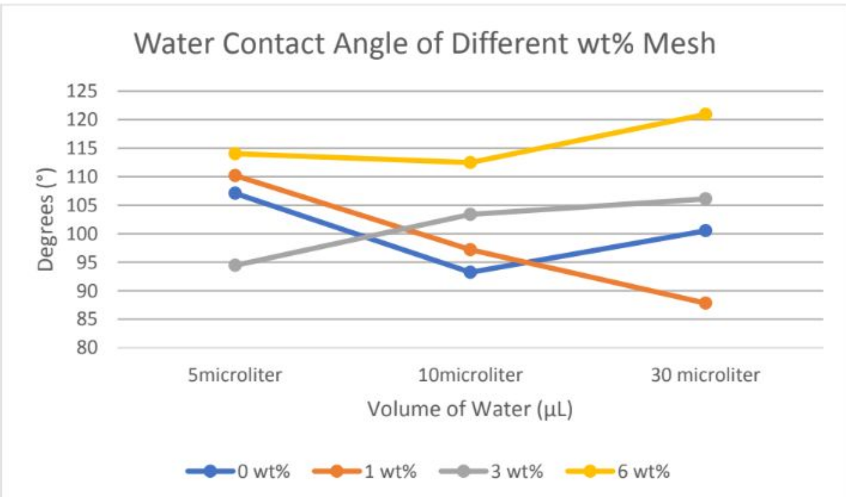

Figure 13. Water contact angles for different CNT wt% and volume of water.

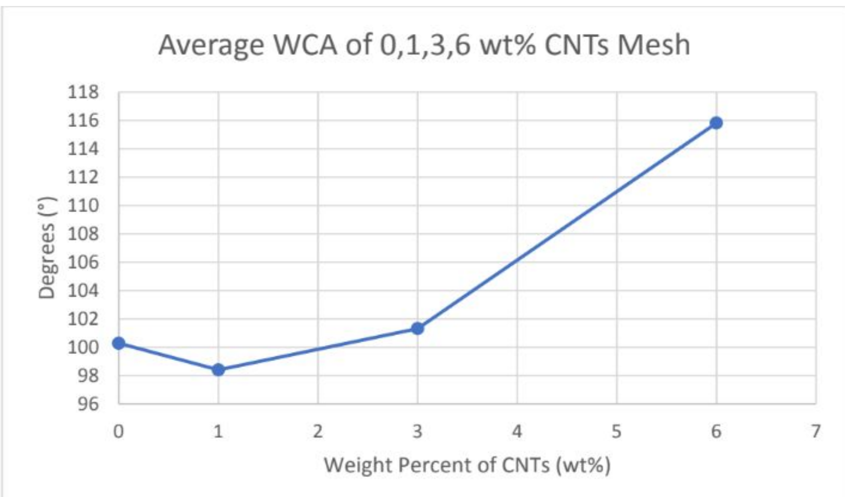

Figure 14. Average WCA of CNT-PDMS Mesh

3D Printed Mesh

After successfully connecting the universal paste extruder with the lulzbot Taz 6, despite having difficulties with the extruder motors, the mesh was printed out and cured. The pores of the mesh were consistently smaller compared to the hand printed mesh. The shape of the mesh was also uniform because of the preprogrammed structure (5x5cm, 0.2-0.3mm pore size). When the water and oil mixture ran through the mesh, the oil flowed through the mesh, and did not push the water through the mesh in doing so. However, the rate of oil flow was extremely slow.

DISCUSSION AND CONCLUSION

The goal of this project is to create a polymer mesh with polydimethysiloxane (PDMS), a silicon-based organic polymer, and carbon nanotubes (CNTs) as the main components to separate oil and water. It also aims to create a method that can easily produce the polymer mesh in large quantities and require less complex synthesis processing.

During the initial trials of making the polymer mesh, there were too many inconsistent sized pieces of CNTs suspended in the ink, making it hard to pipette out with a syringe. Another issue is that the CNTs are very light weight, thus will fly everywhere if not handled properly. The purpose of sonicating the CNTs was to homogenize the texture of the ink base. The process was somewhat successful, however there were larger pieces of CNTs that remained unseparated. When the final mixture is loaded into the syringe, a smoother paste is created, yet there were still a lot of blockages that occurred in the syringe due to larger pieces of CNTs, making it harder to produce a consistent mesh shape. A different method was implemented in hopes of creating a finer CNT mixture. The planetary ball mill was used to grind up the larger pieces of CNTs. Although some of the CNTs were unable to be collected off the ??? balls, the particles were much finer with no large pieces left.

The mesh produced after thermal curing was solid yet flexible. It is durable and would not be easily worn out after a few uses for water oil separation. This is shown when water/oil separation tests are done multiple times on the same mesh and is still able to perform well despite the number of repeated uses. However, the shelf-life of the polymer mesh seems to be short. This is shown when water/oil separation tests are done after a few months of the making of the polymer mesh. The efficiency is significantly lower because the polymer mesh could not repel as much water as it did when it was just made.

When the mesh is successfully printed out with a 3D printer, it can be printed in any shape or size to fit the desired surface designed through CAD software.

Different weight percent of CNTs were tested in the PDMS ink (6 wt%, 3 wt%, 1wt%). Initially, the first few meshes made were all too inconsistent in viscosity and were unable to produce the desired shape. The method of sonication was then adopted to make the texture of the CNTs more homogenous, thus making the mesh much smoother. From testing sunflower oil, hexane, and water on the different wt% meshes, the 6 wt% mesh showed the greatest hydrophobic properties. While all wt% exhibited hydrophobic properties, when more CNTs were suspended inside the polymer mesh, the more efficient in water/oil separation the mesh becomes. The 6 wt% mesh held more water before collapsing compared to other wt% meshes. When water and oil is mixed and dropped onto the meshes, all of them were able to keep the water above while letting the sunflower oil and hexane to pass through. Although all contents of the mixture passed through the mesh, it is suspected that the pores of the mesh were too large to effectively suspend the water, thus breaking the threshold of the water tension.

When the mesh is created with a syringe by hand, the pore sizes were not small enough to efficiently trap water and were mostly inconsistent. The pore size created generally ranged from 4mm to 5mm. The desired pore size would be around 1-3mm. By using a 3D printer and programming, it would be easier to create uniform pore sizes on the mesh. However, most 3D printers print filament made of plastic. The ink base that is created with CNT is much more viscous and chunky. One challenge was to create a homogenous textured ink base and the other is to make an extruder that is compatible with the ink. The extruder on a regular 3D printer can be replaced with one that suits the ink. Thus, a universal extruder was printed, assembled, and swapped into another printer by switching the extruder parts. Specific instructions can be found on a 3D printing blog.[15] The extruder body was 3D printed and the other parts were purchased from Aliexpress. Since the extruder parts were 3D printed, they were not as durable but still workable.

After attaching the paste extruder onto the printer with a designed program, the mesh was successfully printed out. The resulting mesh had a better water-oil separation ability than the ones that were hand printed. The difference in performance is due to the increased homogeneity ink and the decrease in pore sizes were smaller with more consistency. Although the rate of the oil separation was slow, it did not allow water to flow through like the other hand printed meshes.

To measure the hydrophobicity of the mesh, a method called the sessile droplet method was used to calculate the water contact angle. Sessile drop meaning a sitting drop that is not in motion [16]. If the angle that the surface comes in contact with the water is greater than 90, then it is hydrophobic; yet when it is less than 90, it is hydrophilic. By looking at the WCA data, it shows that the 6 wt% mesh had the largest angle, meaning that it is the most hydrophobic. However, the control group without any CNTs had a greater contact angle than the other wt% groups. This implies that there was not enough CNTs on the surface, instead were all suspended inside dimethicone (PDMS). However, this data can be inaccurate because since the WCA must be measured on a flat surface, only the back side of the mesh was used. The front side of the mesh shows uneven surfaces that can possibly contribute to the efficiency of water oil separation. Superhydrophobicity is known to be an enhanced effect of surface roughness. When a water droplet is on surface, the liquid will follow surface corrugations and settle on the top, which allows air pockets to be trapped underneath.[17] Shown in figure 16, this can slightly represent the notion that the rough side of the polymer mesh is more hydrophobic than the smooth side. This is also often compared to the Lotus' effect: The lotus leaves have nanostructures that make the surface rough, and thus have superhydrophobic surfaces that cannot get its leaves wet.[18]

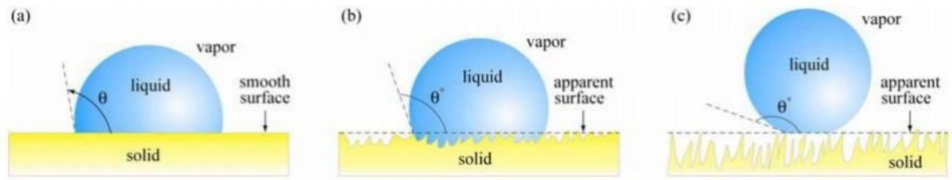

Figure 16. A water droplet resting on a (a) smooth surface, (b) a small rough surface, (c) a large rough surface. [19]

The ideal workings of the polymer mesh is to be hydrophiid and hydrophilic at the same time: water should be repelled completely, while oil should flow through freely. CNTs are hydrophobic in nature and can repel water because they are non-polar. Water molecules are repelled because they are polar and the exterior of CNTs are hydrophobic.[20] There are articles that show that the insides of CNTs can confine water, however, when the CNTs are suspended in dimethicone, only the exterior is exposed, showing only the hydrophobic parts.[21]

Experimental results show that the CNT-polymer mesh can repel water and allow the passage of oils. Although the water trapping efficiency needs improvement, the addition of CNTs do increase the hydrophobic properties of the mesh. As mentioned above, surface roughness of the polymer mesh can increase its hydrophobic properties, suggesting that the higher the wt% of the mesh, the rougher the surface will be. For future work, a wider range of CNT wt% should be tested in PDMS. A greater amount of CNT would increase the hydrophobicity; however, the texture of the ink can become too viscous. Waste oils that are commonly found in the ocean should be used to test in the future, such as crude oil or diesel oil. The formulation of the ink also needs be modified to improve the water trapping characteristics and increase the shelf life. Regarding the slow rate of oil flow for the 3D printed membrane, a possible solution is to test different pore sizes to find an optimal size that can increase and maximize the flow rate of the oil.

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