Research Paper

Water-Oil Separation via PVDF Superhydrophobic/Superoleophilic Membranes

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Abstract

The purpose of this project is to test the effect of carbon nanofibers on superhydrophobicity to create a surface membrane that is both superhydrophobic and oleophilic using Carbon Nanofibers (CNFs). These properties can be used to separate water and oils, which has many potential real-world applications such as inhibiting and cleaning oil spills. The membranes are created via a separation process known as vacuum filtration, which applies a CNF coating onto a membrane. A PVDF membrane was used to separate the CNFs from a Toluene solution to add to the oleophilic attributes of the surface. Four samples of Carbon Nanofibers were weighed (2, 5, 10, and 20 mg) and sonicated for 10 minutes in a test tube with 10 mL of Toluene to evenly disperse the CNFs throughout the solution. The samples were then separated through the vacuum filtration process, leaving a layer of CNFs on the membrane. The contact angle of a water droplet on the surface of each membrane was measured 3 times; this measurement is directly proportional to higher levels of superhydrophobicity. The membrane with the least amount of CNFs (2 mg) was found to have the greatest contact angle (155.1) and lowest slide-off angle (1.5), proving the hypothesis false. This sample was tested with multiple types of oils which were immediately absorbed, indicating that the surface is oleophilic. An Anova test was also performed, further verifying the correlation between Carbon Nanofibers and superhydrophobicity, and rejected the null hypothesis of the variables having no relationship.

Introduction

The Lotus-Effect is the phenomenon commonly found on lotus plants where water will bead up on the leaves due to the plant's nanostructures, causing the surface to be superhydrophobic. Because of the high contact angle and low slide-off angle water forms with the surface, these plants also exhibit no-wetting and self cleaning attributes (Darmanin & Guittard, 2015).

For a surface to be superhydrophobic, it must have a contact angle with the surface that is above 150 degrees, be rough on a nano-scale, and have a low surface energy. By having a rough surface, air is able to fill in the asperities between the nanostructures, suspending the water droplets. Also, there is less contact area between the nanostructures and water. A low surface energy allows for less surface tension (adhesive forces) between the liquid and nanostructures than between the liquid and the membrane. This prevents the water from sticking to the membrane and is the reason for the attributes of high contact angles and low slide-off angles found on superhydrophobic surfaces. There are two distinct models that are associated with superhydrophobicity, the Cassie-Baxter and Wenzel models, known as the slippery state and sticky state respectively. The former model is present when air fills in the asperities between the nanostructures on the surface, whereas the Wenzel state is present when the surface has the optimal contact angle, but because of a high surface energy, water instead fills in the asperities causing higher slide-off angles. The Cassie-Baxter state is the model that is trying to be replicated.

Membrane separation is the process that separates materials through pores or gaps in a molecular arrangement of a continuous structure (Celia et al., 2013). This technology consists of either a porous or dense barrier that may permit the passage of certain compounds selectively in a fluid**.**

Membranes used in separation are commonly designed for superhydrophobic (Surface Contact Angle > 150 degrees) or hydrophilic (Surface Contact Angle < 30 degrees) purposes to promote or prohibit the transportation of water respectively (Johnson 1). There are many different uses and applications for hydrophobic membranes such as filtration, pervaporation, membrane distillation, and more. A big issue that these membranes have the potential to remedy are oil spills which are detrimental to the environment (Sheanan). To accomplish this, a surface membrane that can absorb the harmful oils while at the same time allow the water to become the retentate must be created. This requires the membrane having superhydrophobic and oleophilic properties (Chandler 1).

For this task, Polyvinylidene (PVDF) membranes were coated with varying quantities of carbon nanofibers (CNFs) to test their superhydrophobic and oleophilic properties. CNFs are nanostructures that can create a rough surface on a microscopic level, and have a low surface energy, making them ideal for water-oil separation. The PVDF membrane in particular was used for its oleophilicity, which was further enhanced by the CNFs. These membranes were created via a process known as vacuum filtration where the CNFs were initially mixed into a solution with Toluene and separated through the membrane, allowing them to be deposited on the membrane creating the CNF coating.

Materials

- Varying Quantities of Carbon Nanofibers
- Scale
- 20 mL Test Tubes
- Toluene
- Sonication Device
- Ice Water
- Buchner Funnel
- Buchner Flask
- Vacuum Fume Hood
- PVDF Membranes
- Contact Angle Measurement Device
- Tweezers
- Different Oils

Procedure

1.) Begin by measuring out four samples of Carbon Nanofibers (CNF) that are 100 micrometers long and 150 nanometers in diameter **(Figure 1)**. These samples consist of varying amounts of CNFs: 2 mg, 5 mg, 10 mg, and 20 mg.

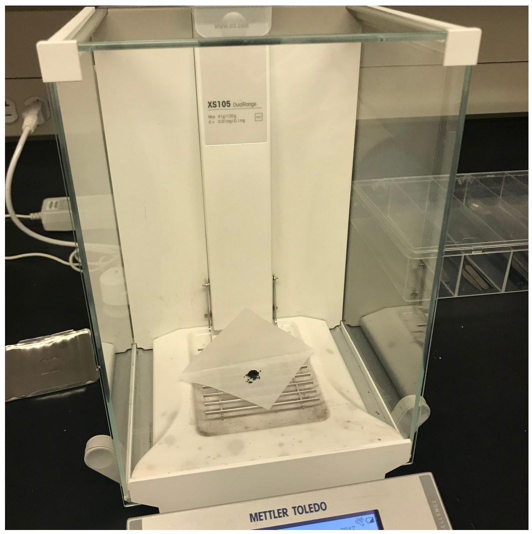


Figure 1: 2 mg of CNFs being measured out

2.) Each sample is placed in separate 20 mL test tubes.

3.) Add 10 mL of Toluene into each test tube with the CNFs.

4.) Prepare the Sonication Device by filling it with ice water until it is mostly full.

5.) Place a test tube with the mixture of Toluene and CNFs on a clamp and put it in the Sonication Device with the Toluene level with the water. This device is used to evenly disperse the CNFs in the Toluene added previously **(Figure 4)**. Sonicate it for 10 minutes and repeat the process for the other samples **(Figures 2 & 3)**.

Figures 2 & 3: The test tube with Toluene and CNFs in the Sonication Device

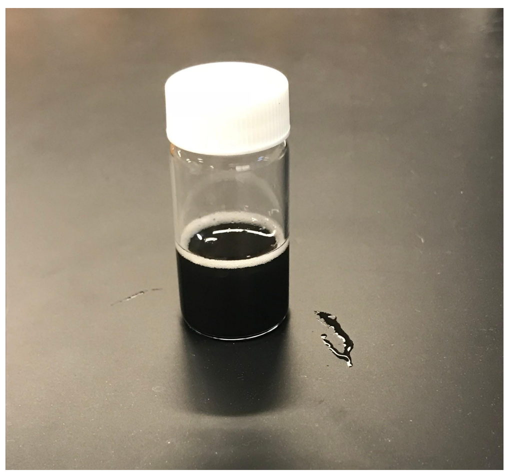


Figure 4: 2 mg of CNFs dispersed in 10 mL of Toluene

6.) Set up the Vacuum Filtration by placing a Buchner Flask in a vacuum fume hood and insert a rubber bung in the top of the flask. Then insert the Buchner Funnel into the rubber bung and place the PVDF membrane in the funnel. Attach rubber tubing from the aspirator to the flask and start the vacuum. The composition can be seen in **Figure 5**.

Figure 5: This is the Vacuum Filtration setup where the Toluene is being separated from the PVDF membrane

7.) Pour out the test tube containing the mixture of Toluene and CNFs into the Buchner Funnel. The dispersion will deposit the CNFs onto the PVDF membrane and separate the Toluene **(Figure 6)**.

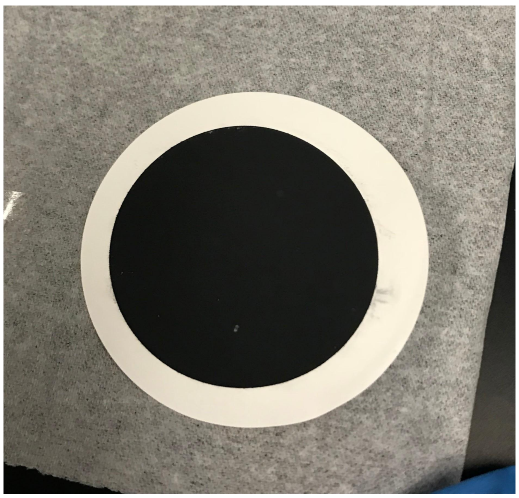
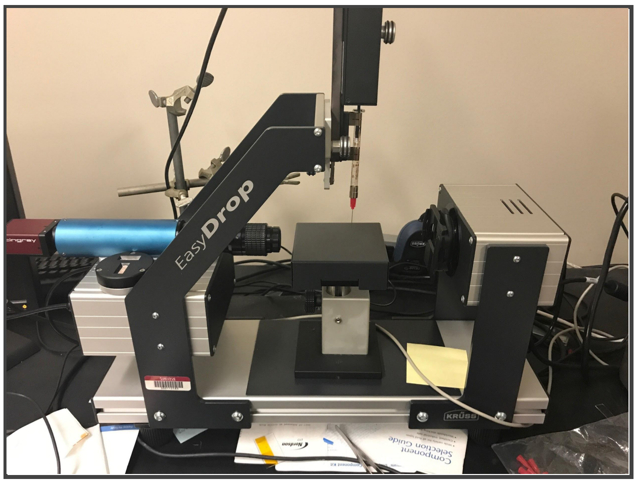
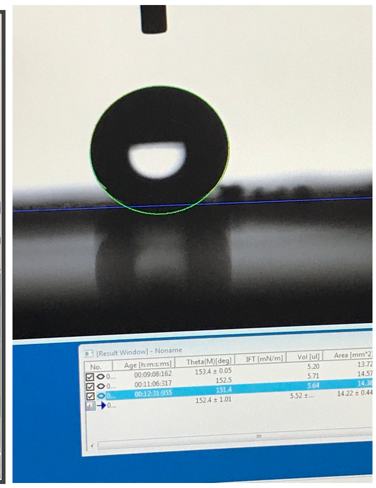


Figure 6: The PVDF membrane with the CNFs deposited on it

8.) Measure the Contact Angle of the Filter Membrane containing the CNF solid by placing a water droplet on the membrane surface and use a contact angle measurement device to measure the contact angle the water droplet forms with the surface. Repeat this with a new water droplet three times for a better average.





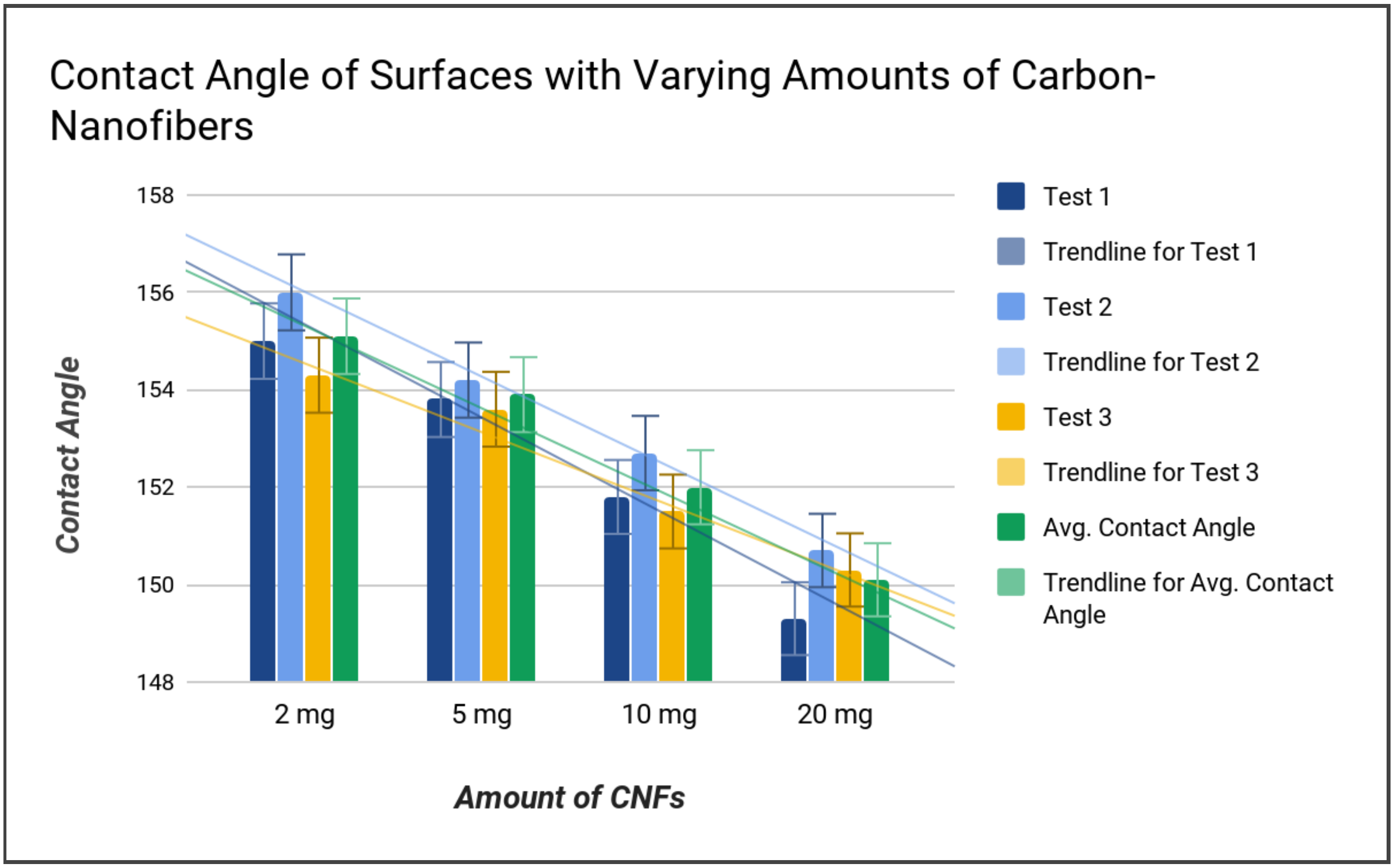
Figures 7 & 8: The contact angle measurement device and its program can be seen above

9.) Repeat this process for the other four samples.

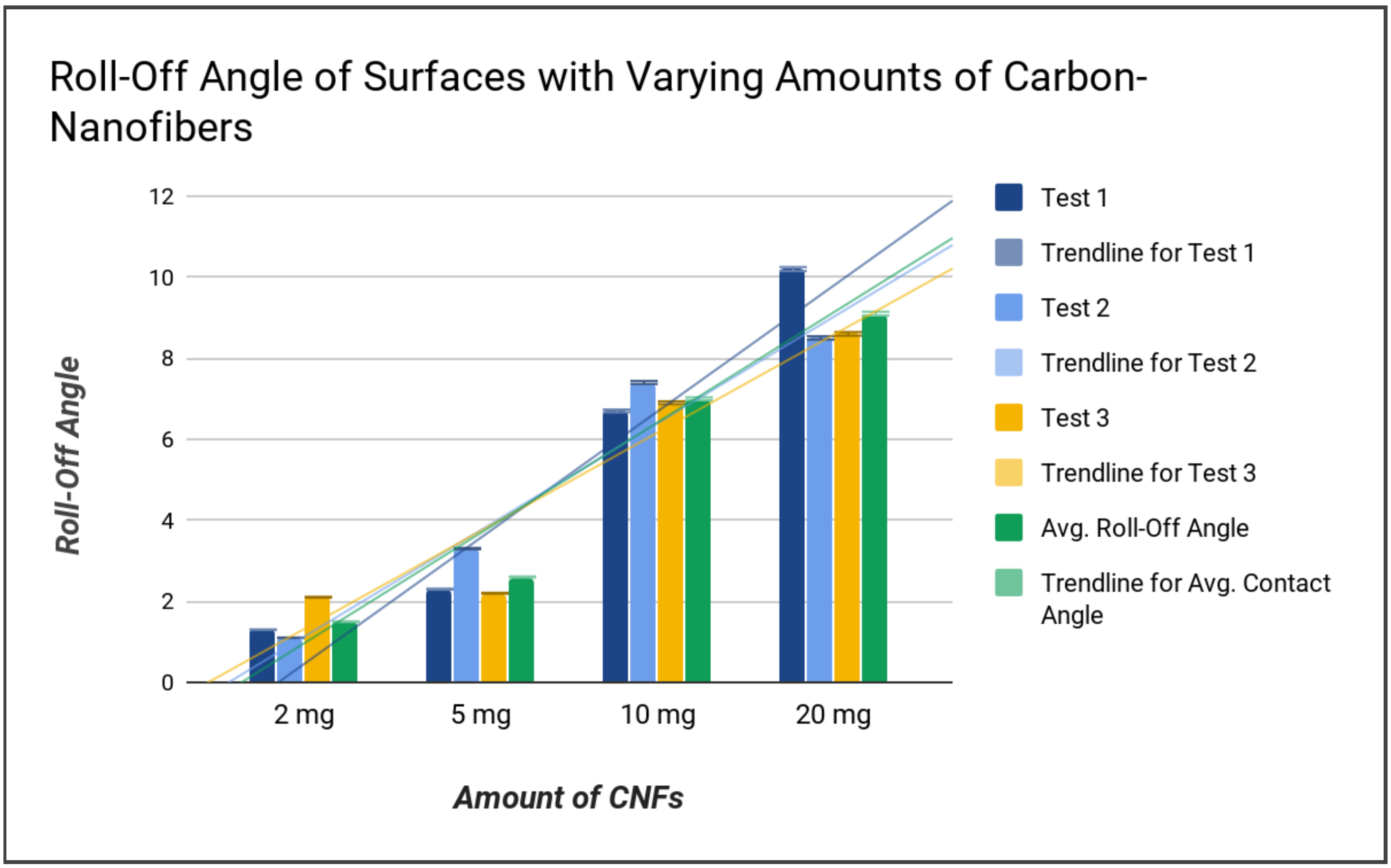
10.) Take the best sample of the five CNF Filter Membranes based on the results (highest average contact angle) and use four different types of oil to measure its oil droplets to test its oleophilicity. If the oil is absorbed, the surface would then be oleophilic and superhydrophobic.

Tables and Graphs

Amount of CNFs in Solution	2 mg	5 mg	10 mg	20 mg
Test 1	155	153.8	151.8	149.3
Test 2	156	154.2	152.7	150.7
Test 3	154.3	153.6	151.5	150.3
Avg. Contact Angle	155.1	153.9	152	150.1



Slide-off Angles of Water Droplets vs. CNF Amount	2 mg	5 mg	10 mg	20 mg
Test 1	1.3	2.3	6.7	10.2
Test 2	1.1	3.3	7.4	8.5
Test 3	2.1	2.2	6.9	8.6
Avg. Slide-Off Angle	1.5	2.6	7	9.1



	1	2	3	4	Total
N	3	3	3	3	12
$\sum X$	465.3	461.6	456	450.3	1833.2
Mean	155.1	153.8667	152	150.1	152.7667
$\sum X2$	72169.49	71025.04	69312.78	67591.07	280098.38
Std.Dev.	0.8544	0.3055	0.6245	0.7211	2.0566

This is the Anova test comparing the contact angle formed between the water droplet and the amount of Carbon Nanofibers used to make the membrane. The p-value for this test is less than 0.000074, justifying that there is a highly significant difference between the groups, proving my null hypothesis incorrect. Also, by having an f-ratio value of 33.12308, the results are significant and there is a variance in data (not random).

	1	2	3	4	Total
N	3	3	3	3	12
$\sum X$	4.5	7.8	21	27.3	60.6
Mean	1.5	2.6	7	9.1	5.05
$\sum X2$	7.31	21.02	147.26	250.25	425.84
Std.Dev.	0.5292	0.6083	0.3606	0.9539	3.3003

This is the Anova test comparing the slide-off angle of the water droplet and the amount of Carbon Nanofibers used to make the membrane. The p-value for this test is less than 0.0001, justifying that there is a highly significant difference between the groups, proving my null hypothesis incorrect. Also, by having an f-ratio value of 91.85799, the results are significant and there is a variance in data (not random).

Results

According to the data, as the amount of CNF used to filtrate the membrane during membrane separation decreases, higher levels of hydrophobicity and oleophilicity are produced. The filter membrane with the least amount of CNFs coated (2 mg) had the highest average contact angle and the lowest slide-off angle. The contact angle of the water droplets on this first filter membrane had an average contact angle measurement of 155.1 degrees from the three different water droplets tested. This means that the surface was superhydrophobic because the static contact angle was over 150 degrees. This is due to there being less contact area between the water droplets and CNFs so the water doesn't stick to the surface as well as samples with higher amounts of Carbon Nanofibers. Because the surface that's created is more rough than the filters created with more CNFs deposited, it allows for more areas where air is able to fill in the asperities between the nanostructures as seen in the Cassie-Baxter model. With the addition of CNFs, a smoother surface was created via the vacuum filtration process, decreasing the superhydrophobicity of the filter membranes. Carbon Nanofibers also have a low surface energy so there are fewer adhesive forces between the surface and the water. By adding CNFs, the surface energy would also have increased, increasing these adhesive forces making the surface "stickier".

The lowest average slide-off angle of the water droplet was also on the filter membrane with 2 mg of CNFs. The membrane experienced an average slide-off angle of 1.5 degrees, also demonstrating how the Cassie-Baxter, or slippery, model was achieved with a really low slide-off angle. The water droplet is suspended on the air filled in the area between the nanostructures, allowing for low slide-off angles, hence causing the slippery state.

This “super-membrane” was finally tested with different oils to test its absorbance capabilities. The membrane with 2 mg of Carbon Nanofibers was able to instantly absorb oils such as ethanol, hexadecane, and petroleum hydrocarbons completely, proving its oleophilic properties.

An Anova was also conducted to test for variances in the data for both tests and the p-value came out to be less than 0.0001 which made the results significant and not random as it was significantly less than 5% error causing rejection of the null hypothesis.

Discussion

The hypothesis and null hypothesis for this experiment were proven incorrect as there was a negative correlation between the amount of Carbon Nanofibers used to create the filter membrane and the superhydrophobicity of the surface. The wettability of carbon nanofibers base coatings are changed based on the amount of CNFs in the solution; according to the data, as the amount of Carbon Nanofibers increased, the superhydrophobicity due to the surface contact angle decreased. The oleophilicity of the membrane was evident as well when the filter membranes containing the most Carbon Nanofibers was tested with four different types of oils as the oil droplets were immediately being absorbed. Through this project, I was able to fabricate superhydrophobic CNF based coatings on Polyvinylidene (PVDF) membranes using simple and affordable techniques. The materials used for this research project were inexpensive and raw materials, such as the carbon nanofibers used and the process of vacuum filtration to create the filter membranes. These CNF coated membranes are also oleophilic (oil-attractive) and able to absorb many types of oils like hexadecane and petroleum hydrocarbons instantly

In the real world, there is a big niche for water-oil separation research. Oil spills are major issues that are really harmful to the environment, an issue that can be solved more efficiently with a surface that can absorb the oils while repelling water at the same time. As the population continues to rise, there will also be a growth in fuel and oil use, which increases the risk for chemical leakages. Water purification is another way in which this separation technology can be exploited. With a superhydrophobic and oleophillic filter membrane, the emulsion of oils and water can be easily separated by absorbing the oils and leaving clean water as the retentate.

Acknowledgements

For this experiment, I would like to acknowledge and really thank Dr. Ganesh, and Mr. Ali, my mentors at the University of Arkansas at Little Rock in the Nanotechnology center for assisting me throughout my project, letting me have access to the lab, providing materials and mixing chemicals. I would like to thank my parents for the endless hours of driving to and from the lab as well.

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