

Investigating the use of plastic waste to clear up oil spills

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Abstract

Oil spills and unmanaged plastic waste are serious issues with severe environmental impact, and plastic foams show promise as oil sorbents. Silicon dioxide nanoparticles decorated with Hexadecyltrimethoxysilane(HDTMOS) were physically deposited onto Expanded polystyrene(EPS) and Expanded polyethylene nets(EPE), in an attempt to enhance their performance. The modifications were shown to increase their hydrophobicity, but their oil absorption capabilities were not investigated this year due to time constraints and lab availability due to COVID-19 safe management measures.

1. Introduction

In this modern age, fossil fuels are the most widely used energy source. As much as 10 million tonnes of petroleum products and derivatives are consumed daily worldwide (Abdullah et al., 2010). Due to this large demand for oil, enormous amounts of it are drilled out of the ground and transported around the world to where it is wanted, often by ship. During this transportation or during the extraction process, accidents may occur, spilling large amounts of the oil into the ocean. Approximately 1000 tonnes of oil was spilled into the ocean in 2019(ITOPF, 2019). It is undeniable that these oil spills cause a large impact on the environment. The oil coats the plumage of seabirds, rendering the creatures unable to take flight and float, causing them to starve or drown. The oil also affects the insulation ability of their feathers, causing many more to die from hypothermia (Nasar & Jones, 2012). Oil spills also cause significant harm to animals under the surface. Toxic oil compounds can poison the small and vulnerable young of the fish, either killing them immediately or causing all kinds of devastating effects as they grow up, having long-term effects on the fish population (Langangen et al, 2017).

3 of the currently used methods of dealing with oil spills include: in-situ burning, oil dispersants and bioremediation. However, bioremediation takes very long(Dave & Ghaly, 2011), in-situ burning releases harmful pollutants, such as carbon monoxide, sulfur dioxide, nitrogen dioxide and particulate matter (Fritt-Rasmussen et al., 2012), and the use of dispersants are expensive and not environmentally friendly (Page et al., 2002).

Plastics are one of the many products produced from petroleum. First invented in 1862, there are now a wide variety of types, with numerous different uses such as packaging, construction and textiles, and as components in electronics (Gilbert, 2017). One type of plastic products are plastic foams. By heating and blowing air into plastic resin, foams of thin cells filled and surrounded with many air spaces can be produced (Altan, 2018). Due to the many air spaces, they have low-densities and reduced thermal conductivity and yet are reasonably strong (Altan, 2018). Therefore, they are popular for purposes like thermal insulation, fireproofing, and for packaging (Altan, 2018). Familiar sights such as the expanded polystyrene foam used in packaging electronic products and for keeping drinks and ice cream cool, the extruded polystyrene foam (styrofoam) used for packing food and even the expanded polyethylene nets which are used to protect fruits from damage demonstrate how widely used they are. However, as much as 8.3 billion tonnes of plastics had been produced globally by 2015. Between 1950 and 2015, 9% of plastic waste was recycled, 12% was incinerated, and the remaining 79% has accumulated in landfills and the environment (Geyer et al., 2017). The discarded plastic items result in land and marine pollution, accumulating on sandy beaches and the seabed, as well as in mangrove forests, and coral reefs (NOAA, 2016). The chemical structure of most plastics renders them resistant to degradation, and as a result, they are slow to degrade. Moreover, low price and durability resulted in a high level of production of plastics. Together, these two features have brought about a high prominence of plastic pollution in the environment.

In an attempt to alleviate both issues at once, studies have started to investigate the secondary use of plastic foam waste as an oil sorbent material for cleaning up oil spills (Patil et al, 2018; Yu et al, 2019). Because plastic foams are organic polymers made from petroleum, they are by nature hydrophobic and oleophilic (Patil et al, 2018). This allows them to absorb less water and more oil, wasting less space and rendering them more effective in cleaning up oil spills on water. Furthermore, since they are highly porous, they can absorb large amounts of spilled oil per unit mass. Studies have demonstrated the effectiveness of such foams as sorbent material for oil spills (Patil et al, 2018; Nasir & Hameed, 2014).

Last year, the authors of this study investigated the performance of expanded polystyrene (EPS) and expanded polyethylene nets (EPE) as an oil sorbent and attempted to improve their performance by applying a stearic acid coating on the plastic foam wastes. Both the plastic foams were hydrophobic and had oil absorption capacities of 12.8g/g and 8.3g/g in a pure oil environment, but it was discovered that the stearic acid coating only increased their hydrophobicity and not their oil absorption capacities. As such, the authors

wished to attempt another method to improve their performance, in order to increase both its hydrophobicity and its oil absorption capacity.

Xu et al. (2018) deposited silicon dioxide nanoparticles decorated with 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PTES) onto corn straw, utilizing the highly hydrophobic fluorocarbon chain on the PTES molecule to render the corn straw hydrophobic and oleophilic. Their product had a water contact angle of 152° and a water contact angle of 0° , as well as a higher oil absorption capacity than the unmodified corn straw. Therefore, the authors wished to apply this method on plastic foams. However, PTES is a highly toxic compound which is a suspected carcinogen and a reproductive toxin (Sigma-Aldrich, 2021), so in this study the hydrophobic modifier was changed to hexadecyltrimethoxysilane (HDTMOS), which has been used in other studies as a hydrophobic modifier. (Zang et al, 2016).

2. Objectives and hypotheses

The objective of this study was to investigate the effect of the HDTMOS modification on the hydrophobicity and the oil absorption capacities of expanded polystyrene and expanded polyethylene nets. The hypotheses put forth were as follows:

1. The HDTMOS coated silicon dioxide particles will enhance the hydrophobicity of both types of plastic foam waste. 2. The modified plastic foam waste will have larger oil absorption capacities than the unmodified plastic foam waste in both a pure oil environment and in a simulated oil spill.

3. Materials and Methods

Plastic foam waste

Expanded polystyrene was obtained as leftover packaging material for appliances and other delicate goods (Fig. 3.1). Leftover expanded polyethylene nets were taken from fruit stalls in wet markets (Fig. 3.2). They are shown in their uncut forms below.



Figure 3.1 Expanded polystyrene (EPS) Figure 3.2 Expanded polyethylene nets (EPE)

Chemicals

Sodium chloride, magnesium chloride, magnesium sulfate, calcium sulfate, potassium chloride and anhydrous sodium sulfate were all purchased from GCE chemicals, while tetraethoxysilane (TEOS) and hexadecyltrimethoxysilane (HDTMOS) were purchased from Sigma-Aldrich. Diesel oil was obtained from the petrol station and found to have a density of 8.27g/ml, and deionised water was prepared in the laboratory.

Equipment

The equipment we used and their models were as follows: Centrifuge (Beckman Coulter Allegra X-22), Fourier Transform Infrared Spectroscopy (FTIR) spectrometer (Bruker) and Microscope camera & Software (Dinocapture).

Preparation of plastic foam waste

0.2g of plastic foam waste was used per sample. The expanded polystyrene (EPS) was broken into 3 cubes of similar size with a total mass of 0.2g (Fig. 3.3) for each sample, while the expanded polyethylene nets (EPE) were cut into diamond shapes (Fig. 3.4), with 0.2g of the diamond shaped pieces per sample.

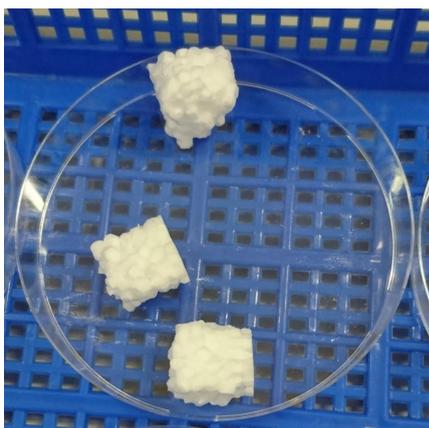


Figure 3.3 A sample of EPS



Figure 3.4 A diamond-shaped piece of EPE

Measurement of water contact angle

Water contact angles of the plastic foams in both their modified and unmodified forms were measured to better understand their hydrophobicity. To do this, a drop of deionised water was placed onto a level surface of the plastic foam piece. Then, an image of the droplet was captured with a microscope camera, and the water contact angle measured with dinocapture software as shown in Fig. 3.5.

Water absorption

As a further test of hydrophobicity, an evaluation of the water absorption capacities of the plastic foam waste had been planned. 50ml of deionised water would have been measured out using a measuring cylinder and transferred into a beaker, and a sample of plastic foam waste placed inside. Because the porous plastic foam floats, a smaller beaker would have been placed into the larger one over the plastic foam waste to keep it fully immersed in the

water as shown in Fig 3.6. The setups would then be left for 1 hour, after which the smaller beaker would be removed, and the plastic foam waste pieces taken out using a pair of tweezers and weighed on an analytical balance. Triplicates would have been done for each type of plastic foam waste-unmodified EPE, modified EPE, unmodified EPS and modified EPS.

However, due to time constraints and lab availability this year, the water absorption tests were not done for the modified plastic foam waste.

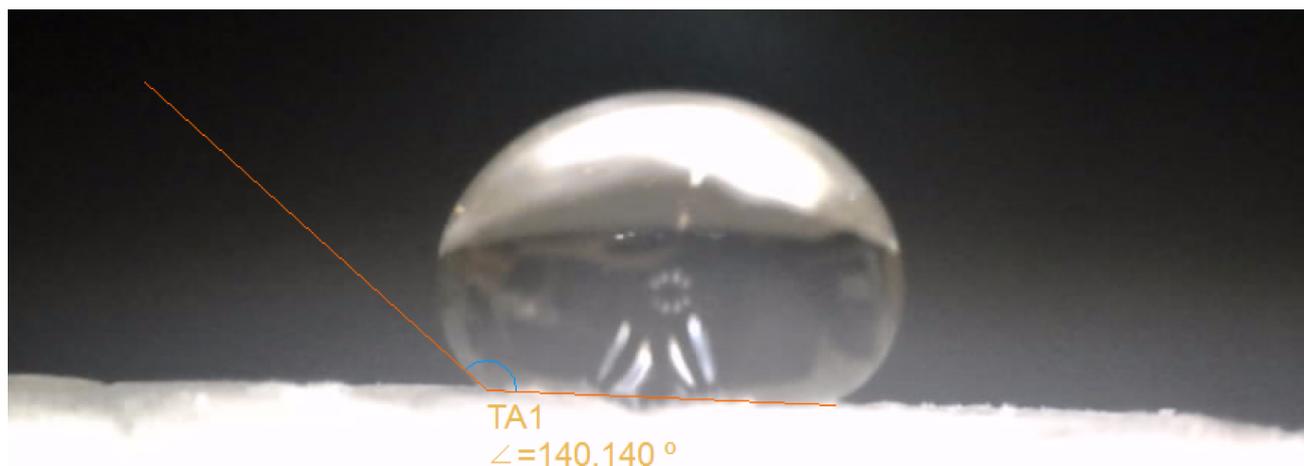


Figure 3.5 Measurement of water contact angle

Modification of the plastic foam waste

This method of modifying the plastic foam waste was based on that by Xu et al(2018). Firstly, to prepare the silicon dioxide particles, 2.5 mL of aqueous ammonia (25% wt, as a catalyst) was added dropwise into a glass bottle containing 45 mL ethanol, 10 mL tetraethoxysilane and 5 mL deionized water. The solution was stirred vigorously for 2 h at room temperature as shown in Fig 3.7. Next, the mixture was left overnight. Homogeneous SiO₂ particles were then separated from the white suspension formed by centrifugation in ethanol at 13000 rpm for 5 min in 15ml tubes. The particles were washed with deionised water and then dried at 60 °C in a hot air oven. Afterwards, the solid obtained was crushed to give a fine powder using a mortar and pestle.

To modify the plastic foam waste, 0.60g of the silicon dioxide particles was combined with 60ml anhydrous ethanol, 1.2ml HDTMOS, 2.4ml deionised water and 0.6ml glacial acetic acid in a beaker. Then, a 0.2g sample of plastic foam waste was added to the mixture, along with a plastic vial to push the plastic foam pieces down and immerse them fully in the mixture as they would float. The mixture was stirred at room temperature for 5 hours as

shown in Fig 3.8, then the plastic foam waste was removed with a pair of tweezers and transferred onto a petri dish. The plastic foam waste was left in the fume hood for 4 days then dried in a hot-air oven for a day at 60°C on the 5th day.

Ideally, there should be large amounts of hydroxyl groups on the surface of the silicon dioxide particles. During the modification of the plastic foam waste, the reaction is as follows: The methoxy groups at the end of the HDTMOS molecule undergo hydrolysis to give hydroxyl groups, which react with the hydroxyl groups on the silicon dioxide particles in a condensation reaction, attaching the long hydrophobic alkyl chains of the HDTMOS molecules onto the particles. The now hydrophobic silicon dioxide particles are then physically deposited onto the plastic foam waste, increasing their hydrophobicity and oleophilicity. (Fig 3.9)

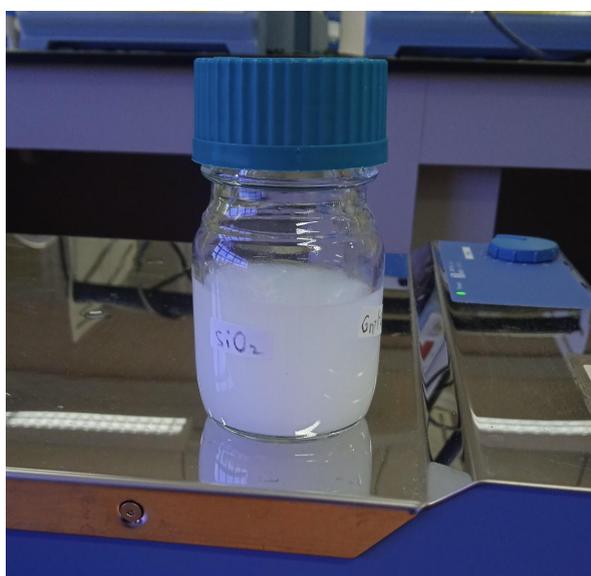


Figure 3.7 Preparation of SiO₂ particles



Figure 3.8 Modification of plastic foam waste

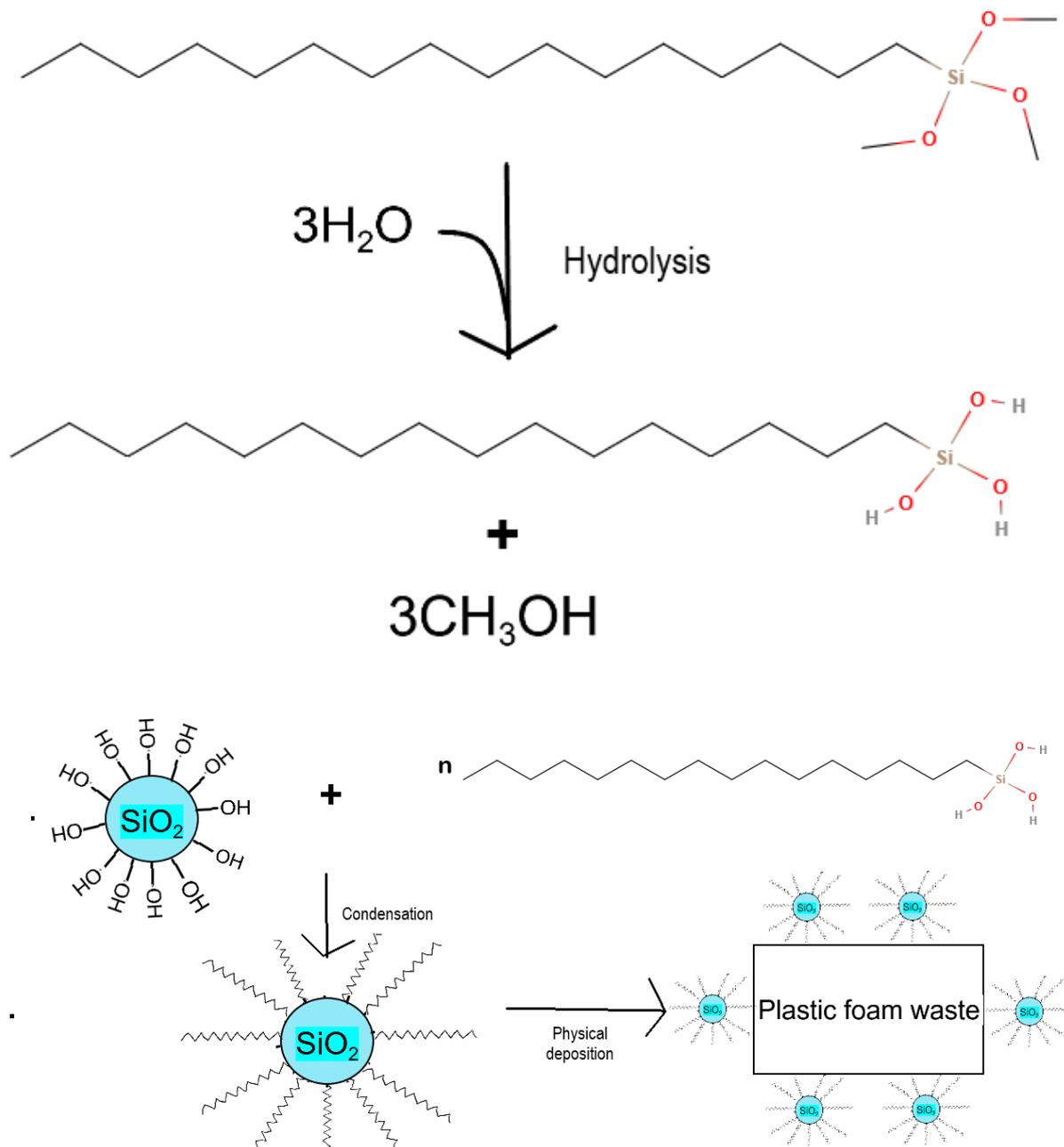


Figure 3.9 Reaction during modification of plastic foam waste

Oil absorption(pure oil environment)

To understand the oil absorption capacities of the plastic foam wastes, this test would have been carried out. In a fashion similar to the water absorption test, a sample of the plastic foam waste would have been placed into a beaker containing 50ml of diesel oil(measured out with a measuring cylinder), and weighed down with a smaller beaker as it would tend to float. The setups would be left for an hour, after which the smaller beaker would have been removed and the plastic foam waste pieces taken out with a pair of tweezers. The mass of the plastic waste pieces would then be measured with an analytical balance. The authors

had planned on doing triplicates for this test for all four types of plastic foam: unmodified EPS, modified EPS, unmodified EPE and modified EPE.

However, the oil absorption test in a pure oil environment for the modified plastic foam waste was not done this year due to time constraints and lab availability due to COVID-19 safe management measures.

Oil absorption(oil-seawater environment)

This experiment was meant to evaluate the performance of the plastic foam waste in a simulated oil spill. Firstly, using the method described by Thio et al. (2012), artificial seawater would have been prepared. This was to be done by dissolving 56 g of sodium chloride, 17 g of magnesium chloride, 8.19 g of magnesium sulfate, 2.5 g of calcium sulfate and 2 g of potassium chloride in 2 litres of deionised water. It was planned that the seawater would be stored in a plastic bottle when not in use in the lab.

For the actual test, 10ml of diesel and 100ml of seawater would have been measured out using measuring cylinders and added into a conical flask. Then, a sample of plastic foam waste would have been added, and the mouth of the flask sealed with parafilm. After this, the setups were to be placed on an orbital shaker and shaken at 150 rpm for an hour to simulate the waves at sea. When the hour is up, the parafilm would have been removed and the mixture poured into a separating funnel(fixed on a retort stand) through a plastic funnel. After waiting a minute for the oil/water to drip down, the plastic funnel and the pieces of plastic foam waste trapped on it would have been removed. 50ml of n-hexane would have been added into the diesel-seawater mixture, having been measured out with a measuring cylinder. The separating funnel would have been capped and shaken, in the process being inverted and having its tap opened to allow the hexane vapour to escape. When this is done, the separating funnel would have been back onto the retort stand and, after allowing the hexane-diesel mixture to separate from the seawater, the seawater would have been drained away into the conical flask used previously. After pouring the hexane-diesel mixture away via the top of the separating funnel into a separate, unused beaker, the hexane extraction process would have been repeated with the seawater to collect any trace amounts of diesel left mixed in it. Then, anhydrous sodium sulfate would have been added to the hexane-diesel mixture and the hexane and diesel would have been decanted into a round bottomed flask, the sodium sulfate being a drying agent to help remove small amounts of seawater left. The hexane would have been removed using a rotary evaporator, and the round-bottomed flasks left in the fume hood to allow any leftover hexane to evaporate away, the mass of the samples being measured until their mass stabilized(indicating that the all the hexane had left). By measuring the mass of the remaining amount of diesel left, the amount

of diesel that the plastic foam waste sample removed would have been inferred. This test has a larger error margin, so it was planned to be repeated 5 times for each of the 4 types of plastic foam. 3 negative control tests with no plastic foam waste involved had also been planned.

However, the oil absorption test in an oil-seawater environment for the modified plastic foam waste was not done this year because of time constraints and lab availability due to COVID-19 safe management measures.

4. Results and discussion

Analysis of silicon dioxide particles

The silicon dioxide particles were analysed using fourier transform infrared spectroscopy(FTIR) to confirm the success of their preparation. The FTIR spectra of the particles is shown in Fig 4.1. The absorption peak at 1101 cm^{-1} and at 797 cm^{-1} were attributed to Si-O-Si asymmetric and symmetric stretching inside the silica respectively (Capeletti & Zimnoch, 2016), while the peak at 955 cm^{-1} was attributed to the stretching of isolated Si-OH on the surface of the particles.(Xu et al, 2018). This shows that there were indeed hydroxyl groups available on the surface of the particles for reaction with the HDTMOS molecules.

Modified plastic foam waste

After being modified, it was found that the silicon dioxide particles were not distributed evenly on the surface of the EPE (Fig 4.2), with visible white patches where the silicon dioxide particles were aggregated. They appeared to be distributed more evenly on the surface of the EPS (Fig 4.3), which generally lacked white patches. The silicon dioxide particles would tend to flake off from the white patches where they were in excess.

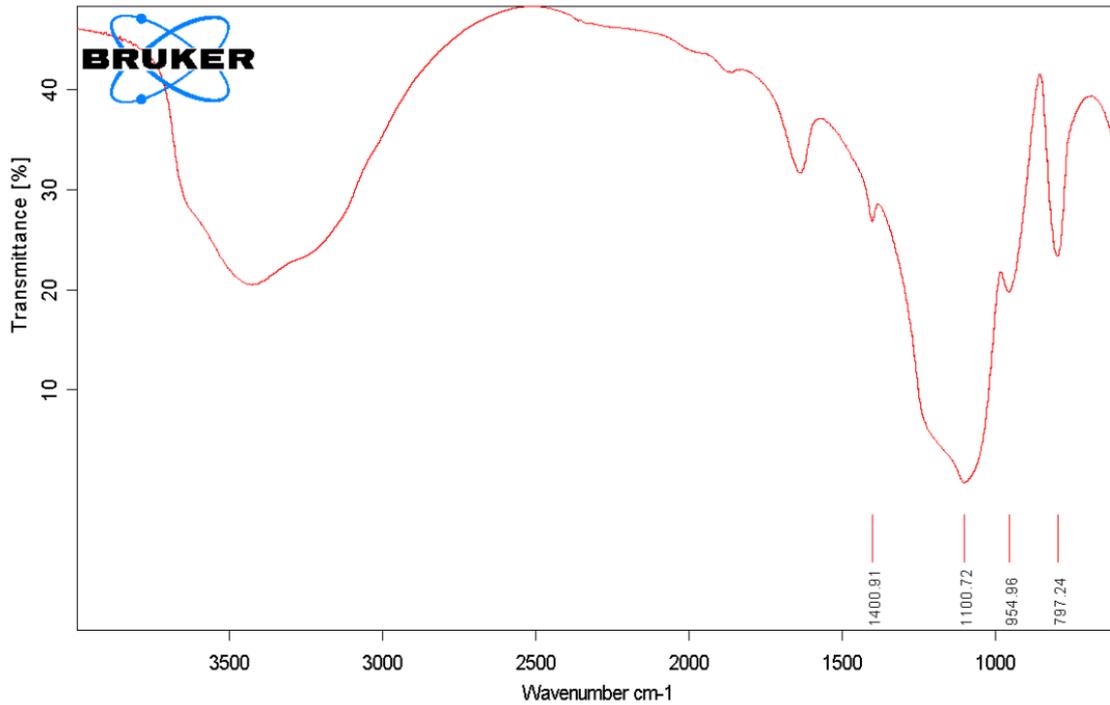


Figure 4.1 FTIR spectra of the silicon dioxide particles.



Figure 4.2 Modified EPE



Figure 4.3 Modified EPS

Water Contact Angle

In their unmodified forms, the EPS and the EPE had water contact angles of 95.5° and 92.8° respectively, on average. After being modified, the water contact angle of the EPS increased to 130.3° , while the water contact angle of the EPE increased to 119.7° , on average.

(Fig 4.4) For comparison, the EPS and EPE coated with stearic acid from last year had water contact angles of 106.8° and 114.5° respectively, on average. (Fig 4.5)

Both types of plastic foam waste were naturally hydrophobic, likely due to the non-polar, hydrophobic nature of the polystyrene and polyethylene polymer molecules they are composed of. The modification improved their hydrophobicity by a considerable degree apparently due to the deposition of the silicon dioxide particles decorated with HDTMOS on

the surface of the plastic foam waste, being more effective than the stearic acid coating done last year. The modification was found to have a larger effect on the hydrophobicity of EPS. However, the modified plastic foam waste was not superhydrophobic (water contact angle $>150^\circ$), unlike the corn straw prepared by Xu et al(2018).

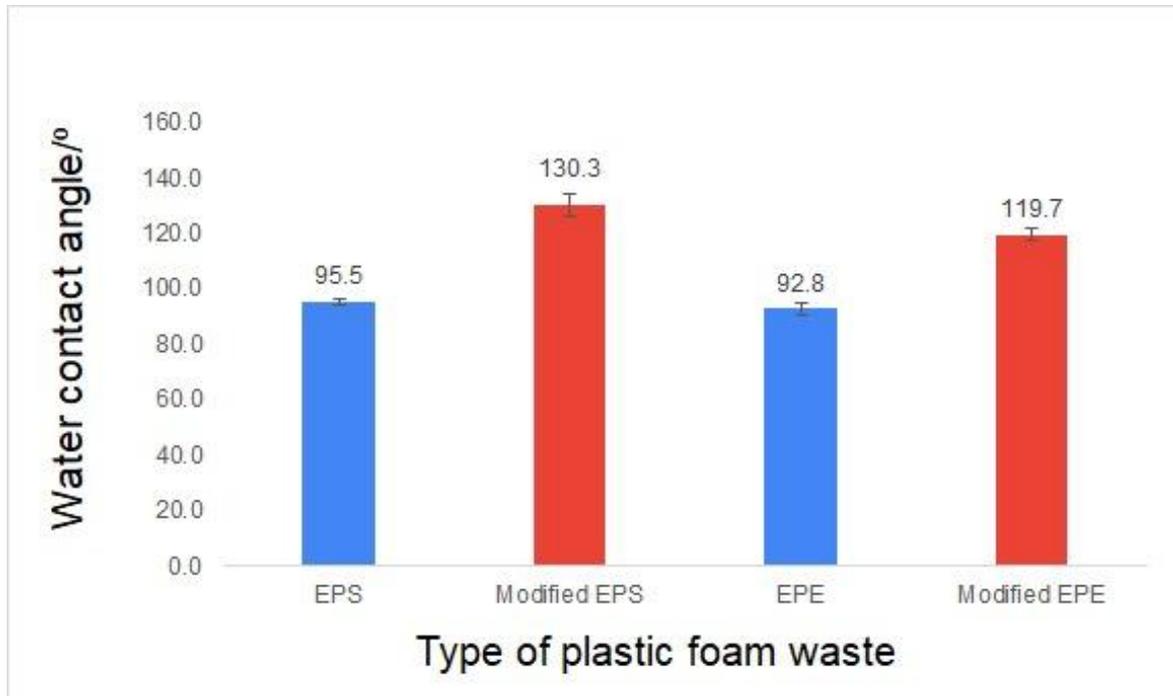


Fig. 4.4. Water contact angle of plastic foam waste (This Year's Work)

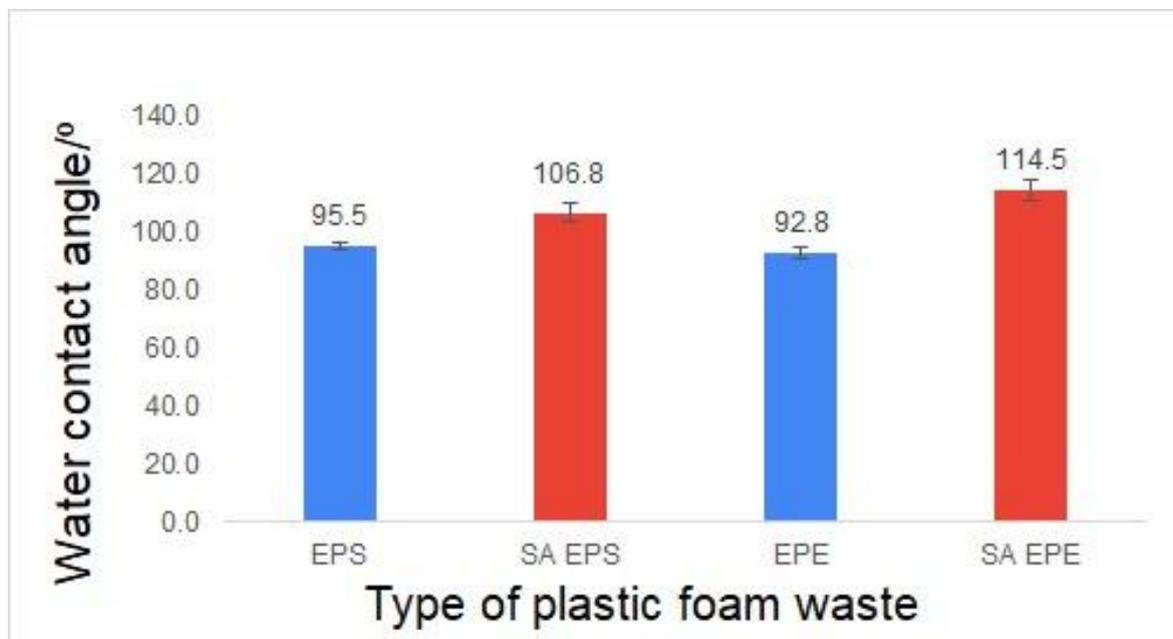


Fig. 4.5 Water contact angle of plastic foam waste (Last Year's Work)

Water Absorption

Due to time constraints and lab availability this year, the water absorption tests were not done for the modified plastic foam waste. Despite this, it predicted that the water absorption

of the modified foam sample would be much lower than the unmodified foam or the foam previously modified with stearic acid, given the significant increase in hydrophobicity as shown in the water contact angle test.

Oil Absorption

Due to time constraints and lab availability this year, the oil absorption tests were not done for the modified plastic foam waste. It is predicted that the modified plastic foam waste will have higher oil absorption capacities than the unmodified plastic foam waste in both a pure oil environment and a simulated oil spill, owing to the superior hydrophobicity of the plastic foam waste, which would increase the strength of the dispersion forces between the plastic foam waste and the oil molecules, facilitating the uptake of oil by the plastic foam waste; while reducing the absorption of water, freeing up for space for the oil in a simulated oil spill.

Limitations

There are some limitations to this study. Firstly, due to the porous, flexible nature of the plastic foams, they could not be cut up/ground up into a powder to mix with potassium bromide for making a potassium bromide disc/pellet. As such, the modified and unmodified plastic foam wastes were not analysed using FTIR, and it cannot be confirmed that the modification of the plastic foam waste proceeded as intended. Secondly, as the silicon dioxide particles were not distributed evenly on the surface of the EPE, the hydrophobicity of the EPE may have varied from one part of the surface to another, affecting the accuracy and precision of the water contact angle measurements. To minimise the impact of this, the water contact angle measurements for the EPE were only done on areas without any white patches, and 6 measurements were taken for both the modified EPS and the modified EPE.

5. Conclusion and Recommendations for future work

In conclusion, it was found that the modification rendered both the types of plastic foam waste, EPS and EPE, more hydrophobic. It is predicted that the modification will also enhance their oil absorption capacities, and the modified EPS is recommended as an oil sorbent as it was more hydrophobic and the coating of silicon dioxide particles on its surface was more stable. For future work, the ratio of the mass of silicon dioxide particles to the reaction mixture for plastic foam waste modification can be reduced to prevent excess deposition on the surface of the plastic foam waste, and a method can be devised to chemically attach the silicon dioxide particles onto the surface of the plastic foam waste to render the coating more stable. Other types of plastic foam waste such as polyurethane foam can also be investigated.

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