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**Super-Hydrophobic High Throughput Electrospun Cellulose Acetate (CA) Nanofibrous
Mats as Oil Selective Sorbents**

A Thesis Presented

by

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Abstract of the Thesis

Super-Hydrophobic High Throughput Electrospun Cellulose Acetate (CA) Nanofibrous Mats as Oil Selective Sorbents

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The threat of oil pollution increases with the expansion of oil exploration and production activities, as well as the industrial growth around the world. Use of sorbents is a common method to deal with the oil spills. In this work, an advanced sorbent technology is described. A series of non-woven Cellulose Acetate (CA) nanofibrous mats with a 3D fibrous structure were synthesized by a novel high-throughput electrospinning technique. The precursor was solutions of CA/ acetic acid-acetone in various concentrations. Among them, 15.0% CA exhibits a superhydrophobic surface property, with a water contact angle of 128.95° . Its oil sorption capacity is many times higher the oil sorption capacity of the best commercial sorbent available in the market. Also, it showed good buoyancy properties on the water both as dry-mat and oil-

saturated mat. In addition, it is biodegradable, easily available, easily manufactured, so the CA nanofibrous mat is an excellent candidate as oil sorbent for oil spill in water treatment.

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Chapter 1. Introduction

1.1 Background of Oil Spill

With the rapid industrialization in the 21st century, oil and petroleum are becoming more and more necessary in our industrial society and also major component of our lifestyle. According to the latest data from U.S. Energy Information Administration (EIA), the total world production of oil and petroleum was about 90.1 million barrels per day (bbl/d) ^[1]. Moreover, about 63% of this amount (56.5 million bbl/d) traveled via seaborne trade ^[2]. Although there are many alternatives as energy use, oil and petroleum are still the main resources for plastics, fertilizers, and chemical feedstock. Thus, it seems that the usage of oil and petroleum will not decrease much in the future.

Oil spill can easily happen due to its heavy use. Since the sources of petroleum can only be found and be produced in some certain regions, the transportation of petroleum such as by pipelines, rails & roads, and barge & ships becomes very necessary. Moreover, the transportation always involves 10-15 transfer points including tankers, pipelines, railcars, trucks and some storage points ^[3]. That is to say, there is a high chance for an oil spill could happen.

A list of the largest oil spill incidents since 1967 is provided in Table 1. Figure 1 and 2 show a trend of the number of large spills (>700 tons) and quantities of the oil spill (>7tons) from 1970 to 2014. Data are derived from the International Tanker Owners Pollution Federation (ITOPF) ^[4].

Table 1: Major oil spills since 1967^[4]

Position	Shipname	Year	Location	Spill size (tonnes)
1	ATLANTIC EMPRESS	1979	Off Tobago, West Indies	287,000
2	ABT SUMMER	1991	700 nautical miles off Angola	260,000
3	CASTILLO DE BELLVER	1983	Off Saldanha Bay, South Africa	252,000
4	AMOCO CADIZ	1978	Off Brittany, France	223,000
5	HAVEN	1991	Genoa, Italy	144,000
6	ODYSSEY	1988	700 nautical miles off Nova Scotia, Canada	132,000
7	TORREY CANYON	1967	Scilly Isles, UK	119,000
8	SEA STAR	1972	Gulf of Oman	115,000
9	IRENES SERENADE	1980	Navarino Bay, Greece	100,000
10	URQUIOLA	1976	La Coruna, Spain	100,000
11	HAWAIIAN PATRIOT	1977	300 nautical miles off Honolulu	95,000
12	INDEPENDENTA	1979	Bosphorus, Turkey	94,000
13	JAKOB MAERSK	1975	Oporto, Portugal	88,000
14	BRAER	1993	Shetland Islands, UK	85,000
15	AEGEAN SEA	1992	La Coruna, Spain	74,000
16	SEA EMPRESS	1996	Milford Haven, UK	72,000
17	KHARK 5	1989	120 nautical miles off Atlantic coast of Morocco	70,000
18	NOVA	1985	Off Kharg Island, Gulf of Iran	70,000
19	KATINA P	1992	Off Maputo, Mozambique	67,000
20	PRESTIGE	2002	Off Galicia, Spain	63,000
35	EXXON VALDEZ	1989	Prince William Sound, Alaska, USA	37,000
131	HEBEI SPIRIT	2007	Taeon, Republic of Korea	11,000

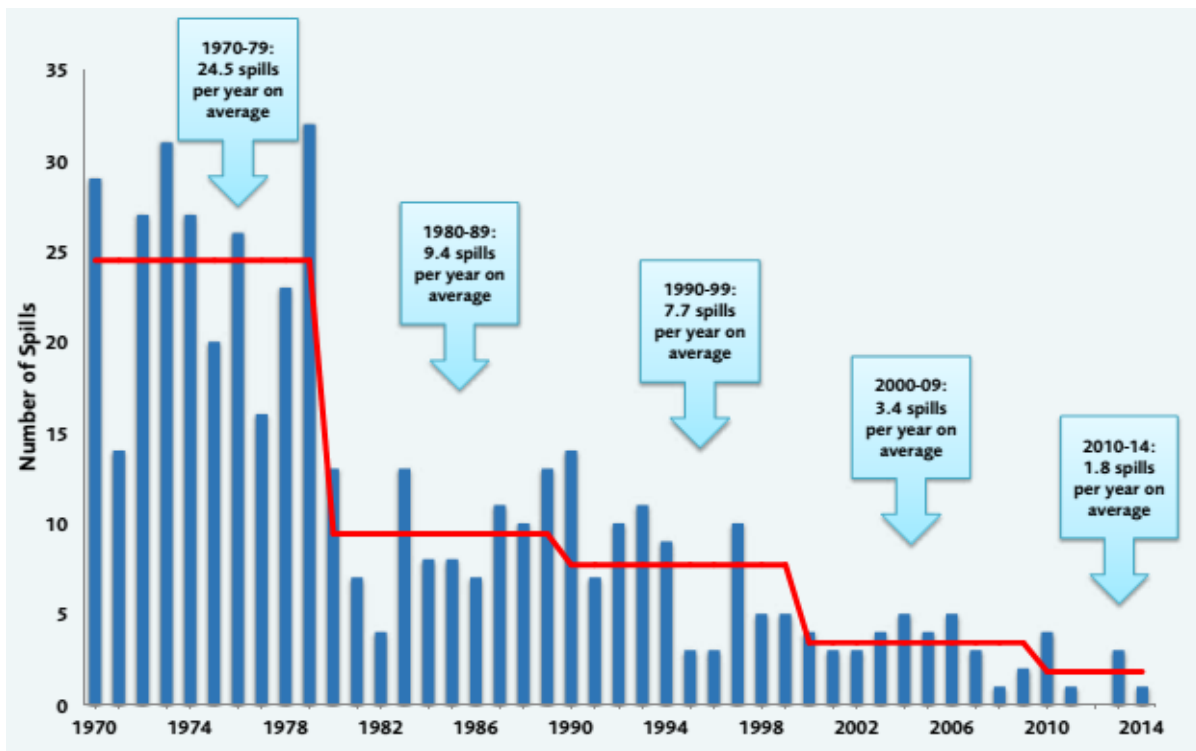


Figure 1: Number of large spills (>700 tons) from 1970 to 2014^[4]

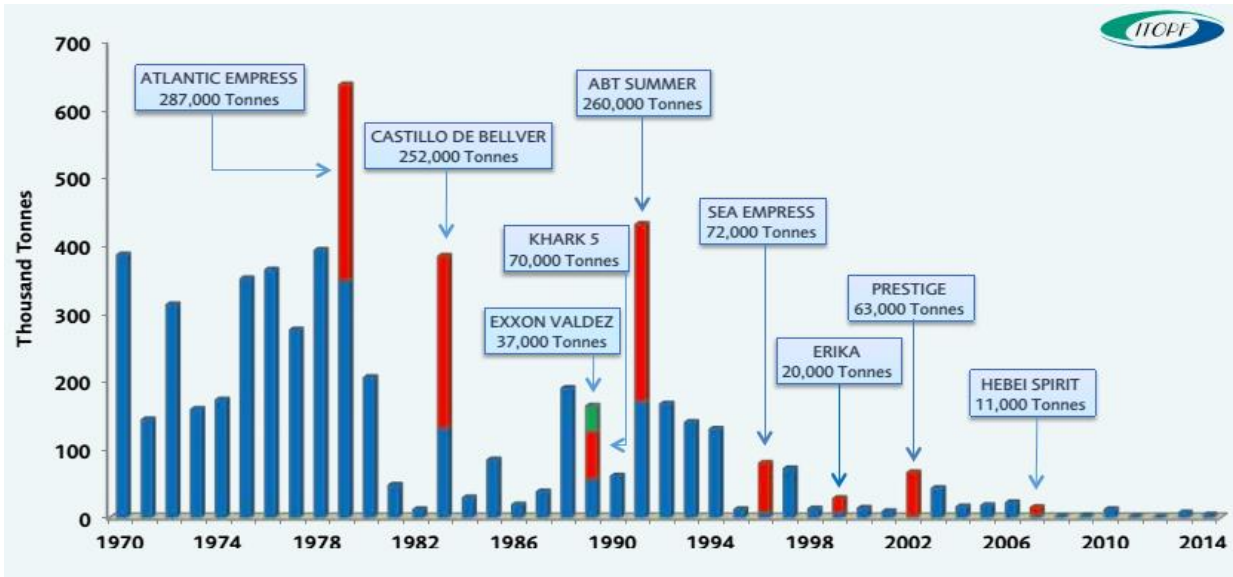


Figure 2: Quantities of oil spilled 7 tons and over, 1970 to 2014[4]

1.1.1 Environmental Impact of Oil Spills

Spilled oil can do great damage to fresh water and marine environments which linked in a complex food chain, even including human food resources. Spilled oil can directly cause physical damages to wildlife and their habitats (such-like birds or mammals’ whole body covered with oil), also can poison some microorganism and thus can destroy the whole food chain [5].

Oil spills in freshwater are more frequent and often more harmful to the environment and human health. This is because that the spilled oil would be more concentrated in freshwater which has confined region and less mobility. Also freshwater directly connects the human domestic water system.

The marine environment is more complex than fresh water. Thus, the oil spill would have a far-reaching influence on the marine ecosystem. Harm to the physical environment will often lead to harm for one or more species in a food chain, leading a damage to other species further

up the chain.

With the technology and equipment development of oil transportation, over the last 25 years, the average number of spills (>7 tons) has progressively reduced by half ^[4]. However, it is still of vital importance to make an immediate response to the oil spill.

1.1.2 Oil Spill Clean-up Methods

Oil spill clean-up is a challenging task. Although the nature can slowly clean up by itself through evaporation, oxidation and biodegradation, it can not deal with big oil spill. ^[6]. Currently, people have developed a variety of effective measures to deal with the oil spills and to minimize its environmental impacts ^[7], as showed in table 2.

Table 2: Common Measures Taken in Response to a Marine Oil Spill

Treatments	Main Purpose	Limitations	Ref
Containment boom	Impeding oil spreading	Not good at high sea states and currents	[8]
Skimming	Scooping up surface floating oil	Not good at high sea states and currents	[9]
Separating oil from water by membrane	Separating oil from water after skimming	Useless for heavy oil	[10]
Burning in-situ	Converting floating oil into gasses & residue	Pollutes the air; works best for thick layers	[11]
Dispersing oil as an O/W emulsion	Breaking up it into small O/W droplets	Increases toxicity & may resurface	[12]
Treating the oil by solidifies	Changing pollutant from liquid to solid	Hard to recover liquid oil	[13]
Building of berms	Confining spilled oil in a small region	Causes damage to the shoreline	[14]

Removal and cleaning of sediments	Removing oil from the shore or bottom	Environment damage; slowing recovery	[8]
Removing with sorbent materials	Absorbing or adsorbing oil	Needs to be collected after being placed	[15]

Containment boom — Using floating containment boom to prevent oil from spreading out over a wider area. This method is strongly limited by the marine condition that the strong current and wave will carry oil either over the top or underneath the barrier ^[8].

Skimming — This method is often used with containment booms. Since most petroleum products can float on water, oil often can be removed from the water surface by using some specialized equipment. Similarly, the marine condition is the main limitation of this method ^[9].

Separating oil from water by membrane — Membrane filtration has been considered as a possible way to separate oil from water. But the membrane always has a filtration for light oil ^[10].

Burning of floating oil in-situ — In-situ burning is a fast way to clean oil spill which can reduce its diffusion and eliminate the need to collect, store, transport, and dispose of recovered pollutant. The problem is that the waste gas after combustion may spread to large area with the wind. Thus, this method is always used when the oil spill happens at deep sea far away from land ^[11].

Dispersing oil as an O/W emulsion — By employing some dispersants to an oil spill to reduce the droplet size, which can make it easier for further treatment. However, the dispersants itself may induce new pollutant ^[12].

Treating the oil with solidifies — Solidifiers can change liquid oil to a solid compound, which is easy for collecting. The most important problem so far is that the solidification rate of these solidifiers are low. Thus, even a moderate sized spill needs a large amount of agent ^[13].

Building of berms — As an oil slick approaches a shoreline, a possible last line of defense can involve piling up the soil into a makeshift dam, i.e. a berm. Nevertheless, a berm is just a temporary solution which can be easily destroyed by storms. This way may disrupt the nature environment of the shoreline ^[14].

Removal and cleaning of sediments — When oil spill happens on ashore, this method can remove or wash the oil-contaminated sand. However, it can only remove some part of spilled oil. And high-pressure water may drive the oil going deep in the sand. High-pressure washing also can accelerate bank erosion and kill organisms ^[8].

Removing with sorbent materials — It can transfer the liquid oil to something solid by incorporated into sorbents, making spilled oil easy to collect. Better than other operations, the sorbent can deal with thin layers of oil. Sorbent materials have the abilities in absorbing many times their weight oil and then can be easily removed from contaminated area. They are easy to be used in any condition and area. Also, most sorbents are environment-friendly and biodegradable ^[15].

1.2 Oil Sorbent

Oil sorbent plays an important role in oil spills clean-up since it has a lot of useful properties which will be discussed below.

1.2.1 Classification of Oil Sorbents

There are mainly 3 types of oil sorbents: natural organic, natural inorganic, and synthetic ^[16].

Nature organic sorbent usually can pick up from 3 to 15 times their weight oil ^[17]. The problem of this kind sorbent is that it also tend to combine with water which causing them to sink. In addition, many nature organic sorbents are loose particles so that it is hard to collect them from the water after using since they would spread everywhere. Here are some examples reported of nature organic sorbents include straw, ground corncob, wood fiber, cotton fiber, kapok fiber, and peat moss, etc.^[18]. They are relatively inexpensive and usually readily available.

Natural inorganic sorbents include clay, perlite, vermiculite, glass, wool, sand, and volcanic ash, etc. ^[19]. They can absorb from 4 to 20 times their weight in oil ^[17]. Generally, the inorganic sorbents and natural organic sorbents are relatively inexpensive and usually readily available, but show poor buoyancy characteristics, low oil sorption capacity and low hydrophobicity.

Synthetic organic sorbents include polymeric materials such as polypropylene and polyurethane foams, are the most commonly used commercial sorbents in oil spill cleanup due to oleophilic–hydrophobic properties [20]. Table 3 shows some examples of studied sorbents and their properties.

Table 3: Examples of 3 types of oil sorbents and their features

Classification	Example	Feature	Ref.
Nature organic sorbent	peat moss carbonized at the temperature of 200-250 °C and modified by acetic acid	high buoyancy and low sedimentation velocity, porous structure allowing them to absorb the oil products well and retain them for a long time	[21]
	C. pent Andra (L.) Gaertn (kapok) exhibited as a natural sorbent.	high hydrophobic–oleophilic characteristics, stability for prolonged use, with higher saturation time and low bed height reduction at higher packing density and higher oil viscosities.	[22]
	silk-floss	showed a rapid oil sorption and a very high sorption capacity of approximately 85 g oil/g sorbent (in 24 h), a high degree of hydrophobicity and low water uptake	[23]
Natural inorganic sorbents	Silica Aerogels	large surface areas, high porosity, low density and low thermal conductivity; the easy collapse of their structure due to adsorption of water	[24]
	Modified geopolymers	can easily prepared from industry waste	[24]
Synthetic organic sorbents	polyvinyl chloride (PVC)/polystyrene (PS) fiber prepared by electrospinning	the sorption capacities for motor oil, peanut oil, diesel, and ethylene glycol were 146, 119, 38, and 81 g/g, respectively; excellent oil/water selectivity, high buoyancy	[25]
	polyurethane sponges treated with silica sol and gasoline successively.	High sorption capacity (100g/g for motor oil), excellent oil/water selectivity, and high reusability	[26]

Although several sorbents have been synthesized which exhibit much better properties than nature sorbent in oil spill clean-up, it is still a challenge to get ideal oil sorbents that could meet oil spill clean-up need.

1.2.2 Properties of Oil Sorbent

Lipophilicity: Lipophilicity is the ability of strong affinity for oils. The oil sorbent materials have the lipophilic substances which tend to dissolve in other lipophilic substances such as fats, oils, lipids, and non-polar solvents like hexane or toluene.

Hydrophobicity: Hydrophobicity is the ability of a material that is tending to repel water. Lack of hydrophobicity may also contribute to sorbent's low oil pick-up ability and may cause a collapse in sorbent microstructure due to water absorption ^[27].

Functional group: A lot of studies showed the hydrophilic and hydrophobic behavior of materials is determined by certain functional groups and its location such as the asymmetric and symmetric aliphatic hydroxyl groups ^[22].

Surface morphology: the Morphological structure of the material is another important factor in the ability of oil up taken for the oil sorbent. For example, kapok shows excellent oil absorption capacity thanks to its micro-tubes or hollow structure which allows more oil in these spaces. In addition, materials like wool and cotton so have the structure of rope or twisted ribbon-like also result in oil absorption ability. And compared to a smooth surface, a rough surface is more likely to absorb oil ^[28].

Pore volume and size: The number and size of pores existed in the structure of sorbent materials also have the effects in oil adsorption. Generally, oil adsorption efficiency will increase with the reduced size of sorbent pore and increased pore number ^[27].

Critical Surface tension: The critical surface tension γ is the highest surface tension when liquids completely wet the surface. Previous findings showed that there is a strong relationship between γ and sorption capacity. In principle, sorbent with low γ has a higher tendency to exclude water and their tendency to float on water ^[7].

Buoyancy: Finally, buoyancy is also an important property when choosing materials as an oil sorbent. Buoyancy is closely related to density and pore volume of the materials. With a bad buoyancy ability, the sorbent will sink to the bottom of the body water with sorbed oil which will harm the environment. The buoyancy ability will decrease with the time when air entrapped between its component fibers or particles. Some study proved that the presence of long and branched hydrocarbon chains in the sorbents may affect its buoyancy ability ^{[7][27]}.

1.3 Nanofiber

1.3.1 Fiber

Fibers exist everywhere in our daily life. Since ancient times, humans have discovered and began to use a variety of natural fibers. Such as cotton, hemp, wool, silk for cloth and other textile materials. Fiber has two apparent geometrical characteristics. The first one is that the proportion of length and diameter is large. The second is the diameter of the fiber must be very thin; it is necessary to appear a certain flexibility ^[29]. Since fiber has this two structural characteristics which result in a lot of useful properties, people showed great interests on

synthetic fibers in modern research. And now compared to natural fibers, synthetic fibers can often be produced very cheaply and in large amounts.

Researchers found that synthetic fibers showed several remarkable characteristics if made its diameter decrease from microns to submicrometer or nanometer ^[30]. Such as very large specific surface area, flexibility, and strong mechanical behavior, which made nanofibers suitable for many important applications.

Nanofibers are defined as solid fibers with a nanoscale diameter and better mechanical performance and flexibility than any other form of the same material ^[31]. There are two classification methods are used ^[29]. One is according to their internal structure as uniform and core-shell nanofibers and the other is according to their orientation as randomly-oriented and aligned nanofibers (Fig. 3).

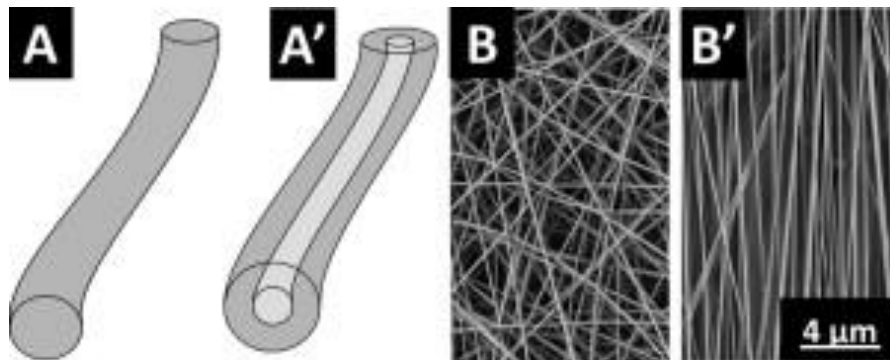


Figure 3: A scheme of (A) uniform and (A') core-shell nanofiber, and SEM images of (B) randomly-oriented and (B') aligned nanofibers^[29]

1.3.2 The Fabrication of Nanofibers

Nanofibers can be produced by using various techniques, such as tensile, phase separation, self-assembly, forcespinning, interfacial polymerization, melt blowing, template melt extrusion,

template synthesis and electrospinning. J. Peli penks et.al. summarized the most commonly used methods for nanofiber production and their scale-up ability, advantages, showed in Table 4:

Table 4: Brief summary of the most commonly used methods for nanofiber production

Method	Scale up	Advantages	Disadvantages
Tensile	×	Simple process.	A limited amount of product discontinuous process.
Forcespinning	✓	Free from high voltage simple method high production yield.	Thermal degradation of melts highly concentrated polymer solutions fibers is usually much thicker than 1 μm in diameter.
Melt blowing	✓	Simple, one-step method, fiber diameter control by an orifice, no need for solvents.	Limited to melted polymers, the high viscosity of melts, the size of the orifice in the die, thermal degradation of melts.
Phase separation	×	Simple, no special equipment required.	Numerous parameters, limited to a few polymers.
Self-assembly	×	Suitable for production of very thin nanofibers.	Poor control over morphology and orientation of nanofibers.
Template melt extrusion	×	No need for solvents, homogenous fiber diameter.	A short length of fibers, time-consuming.
Template synthesis	×	Aligned nanofibers, homogenous and easily controlled fiber diameter.	Complex method.
Electrospinning	✓	Unlimited length simple and core-shell nanofibers easy setup great diversity of polymers and solvents used the one-step method.	High voltage solvents required numerous parameters affecting the process.

Tensile can produce a long single nanometer fiber filament. Fibers are fabricated by contacting a previously deposited polymer solution droplet with a sharp tip and drawing it as a

liquid fiber, which is solidified by solvent evaporation. However, only those viscoelastic material are able to withstand great stress drawing deformation and stretch into nanofibers ^[32].

Phase separation process is very time-consuming. A gel is formed by cooling the polymer solution to the gelation temperature. Afterward, the gel is immersed in distilled water for solvent exchange, followed by removal from the distilled water, blotting with filter paper and transfer to freeze-drying^[33].

The Self-assembly is similar to the phase separation method. Amphiphilic molecules are used as basic building blocks that self-associate to produce nanofibers ^[33].

Forcespinning uses applied centrifugal force in a very highly concentrated polymer solution or melt to produce fibers ^[34].

Melt blowing is the method by using a hot air as an extruding force to squeeze out a polymer melt through an orifice die to the collector, and then cooled to form the fibers ^[35].

Template melt extrusion is similar with melt blowing. The molten polymer is forced by an extruder screw through an anodic aluminum oxide (AAO) membranes in the head of extrusion devices and then cooled to solidify ^[36].

Template synthesis is electrochemical or chemical way to formed nanofibers within the numerous cylindrical pores of a nonporous membrane (AAO) ^[33].

The electrospinning is the only way can directly, continuous to produce polymer nanofibers currently, which has gained a lot of attention in the last few years. It is a simple technique to

produce continuous nanofibers with many outstanding characteristics, such as high porosity, a high ratio of surface area to mass and superior mechanical properties.

1.4 Electrospinning of Nanofibers

Electrospinning is a unique approach to producing fine fibers from polymer solutions or melts. Electrospinning is extensively studied by Zeleny on the behavior of droplet at Taylor cone in 1914 and patented by Formhals et. al. in 1934 ^[37]. Now it is the primary nanofabrication route for polymer fibers. Fibers produced by electrospinning have a thinner diameter (from nanometer to micrometer) and a larger surface area which leading to many different applications.

There are many advantages made electrospinning an outstanding way for the formation of nanostructured composite mats. Such as no special requirements for the processing environment (operated in an ambient environment) and a wide range of appropriate precursor materials (polymers or biologicals) – such as proteins, tissue, etc.

In order to fabricate more complex nanofibrous structures in a more controlled and efficient way, recently a lot of advanced systems have been developed. In this study, a novel high throughput electrospinning system was used, which will discuss later in this article.

1.4.1 The Setup and Process of Electrospinning

A typical electrospinning setup is shown in Figure 4, which consists of a programmable syringe pump, a syringe with needle, a grounded metal collector and a high voltage power supply ^[38].

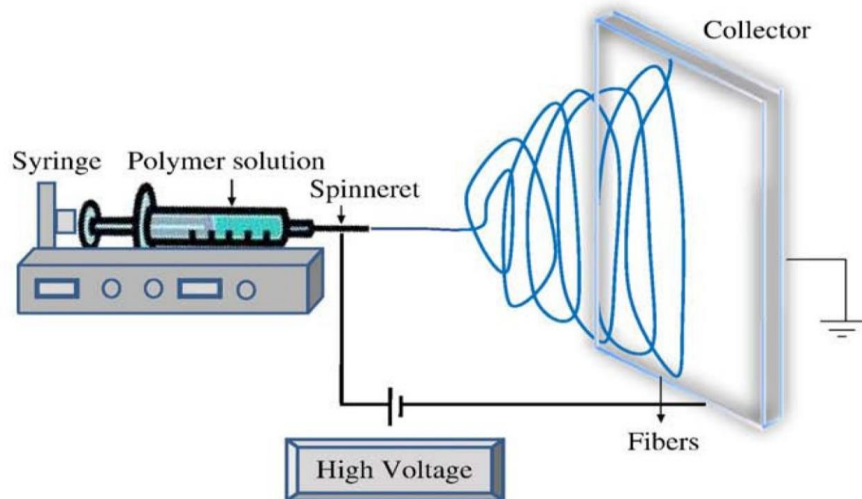


Figure 4: A typical electrospinning setup^[38]

Firstly, polymers are dissolved in some selective solvents to form polymer solution. Then introduce this polymer solution into a syringe for electrospinning.

In the electrospinning process, the polymer solution is pumped out at a fixed rate by the programmable syringe pump. The applied electric field acting on the top of the capillary induces an electric charge on the liquid surface, which weakens the surface tension of the droplet. When the electric field applied reach a critical value, a Taylor cone formed. After the electric field strength overcome the surface tension forces, electrically charged fluid will eject from the top tip of Taylor cone and fly to the collector. During this flight, the electric jet experience a process of acceleration in the injection zone, and at the same time experiencing evaporation, condensation, and highly stretched. Finally, the fibers will be deposited on the collector.

1.4.2 Effects of various parameters on electrospinning

Although basic electrospinning is a simple way to produce fibers, the process is still affected by many different parameters. Thus to get expected products is very challenge. Base on

a lot of studies, the parameters affecting electrospinning can be divided into three major groups: solution parameters, process parameters, and ambient parameters ^[38].

The properties of fibers are determined by their morphology, which results in different application. Despite these parameters always correlated to each other, to get a better understand on the effect of every single parameter is very important.

I. Solution Parameters

a. Concentration- Solution concentration is an important influence on fibers' morphology. According large numbers research ^[38], beads are formed at too low or too high concentration. Generally, as increasing the concentration of the solution, the fiber diameters will be increased.

b. Molecular Weight- molecular weight is a decisive factor for the viscosity of solution since it reflects how many entanglements of the polymer chain exist in the solution. Gupta et al. ^[39] have investigated the effect of molecular weight on electrospinning process by synthesizing different molecular weight PMMA. Their study showed that with the molecular weight increased, the number of beads and droplets decreased.

c. Viscosity- Viscosity is the other crucial parameter in electrospinning process. It mainly related to solution concentration that is to say it determined the minimal concentration of continuous fibers formed. With too low viscosity beads may formed and there is no continuous fiber formation while at too high viscosity result in a difficult stress relaxation for polymer solution, which could prevent the formation of Taylor Cone ^[40].

d. Surface Tension- surface tension is a function of the solution's composition. Generally, too high surface tension may result in an unstable jet or sometimes even droplets may form, which would inhibit the electrospinning process ^[41].

e. Conductivity/Surface Charge Density- In principle, with the increasing of electrical conductivity the diameter size of the fibers would decrease. Solution's conductivity is determined by the polymer itself and solvent type. In addition, Zong et al. ^[42] have demonstrated that by adding ionic salt into the solution there is a drop in beads formation, and the fibers are more uniform and thinner.

II. Processing parameters

a. Applied Voltage- Applied voltage provide electric field and necessary charges in the solution to formed Taylor cone at the tip of the needle. Researchers ^[43] have found that when applying higher voltages will cause increased electrostatic repulsive force on the fluid jet. This would lead a reduction in the fiber diameter. However, with a too high voltage there is also a greater probability of beads formation.

b. Flow rate/Feed rate- Flow rate has a relationship to the time of the solution evaporation from needle tip to collector since it determines the jet velocity. Thus, the optimum flow rate should be low which could provide enough time for the solvent's evaporation ^[38].

c. Tip to Collector Distance- Solvent need time to evaporate from fibers before they reach the collector. The distance between the tip of the needle to collector determine the dry time for fibers. It has been observed that beads may formed if the distances are either too close or too far ^[43].

III. Ambient parameters

a. Temperature- There is an inverse relationship between viscosity and temperature. Mittuppatham et al. ^[44] prepared polyamide-6 fibers with the temperature ranging from 25 to 60 °C and they found that as the ambient temperature is increased, the fiber diameters is decreased.

b. Humidity- Environment humidity has an effect on the evaporation rate of the solution from the tip of the needle. With a low humidity, polymer jets is preferred electrospinning since polymer jets can easily evaporate. Whereas high humidity can cause beads formation ^[45].

1.5 Electrospinning of CA nanofibers

1.5.1 Cellulose acetate

Among others nanofibers materials, Cellulose acetate (CA) had played an important role in many application areas. CA is a derivative of natural cellulose, such as wood fibers or the short fibers (linters) adhering to cotton seeds ^[46]. Figure 5 shows the general chemical structure of CA.

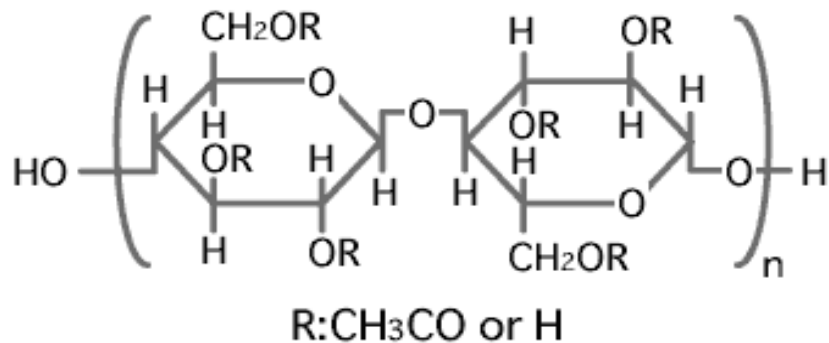


Figure 5: General chemical structure of cellulose acetate^[46]

CA has many excellent characteristics, such as eco-friendly, cheap, comparatively high modulus and adequate flexural and tensile strength, etc.

CA has a wide array of applications in biomolecule immobilization, tissue engineering, bio-sensing, nutraceutical delivery, bioseparation, crop protection, bioremediation and in the development of anti-counterfeiting and pH-sensitive material, photocatalytic self-cleaning textile, temperature-adaptable fabric, and antimicrobial mats, etc. According to a recent report by Global Industry Analysis, the worldwide market of cellulose acetate is projected to about 1.05 million metric tons by 2017 ^[46].

Its good hydrophobic and oleophilic made CA a very suitable candidate as absorbents for oil spill cleaning-up.

1.5.2 Selection of solvent system and process optimization

Electrospinning is the most efficient and simplest technique for producing CA nanofibrous membranes with high surface-to-volume ratio and high surface roughness.

Choosing a solvent system for electrospinning CA fibers is important. B. Ghorani et. al ^[47] and Silvia V. et. al ^[48] have studied a lot of electrospun CA nanofibers with different solvent system which showed in table 5.

Table 5: Results of electrospun CA nanofiber with different solvent system

	solvent system	Ratio	concentration	Average fiber diameter(m)
single solvent system	Acetone	—	15%(w/v)	Few ribbon-like fibers
	DMAc	—	15%(w/v)	Only beads
	Acetic acid	—	15%(w/v)	No production
	Chloroform	—	15%(w/v)	Only beads
	Methanol	—	15%(w/v)	Only beads
mixed solvent system	Acetone: water	17 : 3(v/v)	15%(w/v)	No production
	Acetone: water	4: 1(v/v)	10%(w/v)	Precipitation
	Acetic acid: water	3 : 1(v/v)	15%(w/v)	Large beads
	Acetic acid: acetone	3 : 1(v/v)	15%(w/v)	Few fibers and large beads
	Acetic acid: DMAc	3 : 1(v/v)	15%(w/v)	Large beads
	DMAc: acetone	2 : 1(v/v)	15%(w/v)	Large beads
	Methanol: water	4: 1(v/v)	10%(w/v)	Precipitation
	Methanol: acetone	4: 1(v/v)	10%(w/v)	Precipitation
	Acetone: methanol	4: 1(v/v)	15%(w/v)	Fibers and small beads

Chloroform: methanol	4: 1(v/v)	15%(w/v)	Some ribbon-like fibers
Acetone: DMAc	2: 1(v/v)	15%(w/v)	Fibers and small beads
Acetone: DMAc	2: 1(v/v)	25%(w/v)	Fibers free of beads
DMAc: acetone: water	(32 : 63 : 5 w/w)	15%(w/v)	Fibers free of beads

From this table, we can found that by using the single solvent system it's hard to get fibers. Mixed solvent systems are easier to get fibers than a single system, but still need to find a way to control the beads formation. In this study, a new solvent system has been studied and prepared fine CA fibers by using a novel electrospinning device.

Chapter 2: Experimental Methods

2.1. Materials

All chemicals were used as received without any purification. CA (Aldrich Chemistry, USA) having a molecular mass of 29,000 were utilized in this study. The solvents of the binary system used in this work were acetone (General use HPLC-UV Grade Reagent Grade ACS/USP)/acetic acid (Glacial by ACS reagent grade) with a volume ratio of 2/3 as showed in table 6.

Mixing CA and the acetone/acetic acid binary solvent in room temperature with a series of different concentration which are 10.5%, 12.0%, 13.5%, 15.0% (w/v). Then ultrasonic agitation was performed for 2 hours, and the sol was allowed to settle for 20 hours until CA completely dissolved and homogeneous solutions were obtained.

Table 6: Recipe of 10.5%, 12.0%, 13.5%, 15.0% (w/v) solution

Concentration (w/v)	CA(g)	Acetic Acid(ml)	Acetone(ml)	Total Volume(ml)
10.5%	1.575	9	6	15
12.0%	1.800	9	6	15
13.5%	2.025	9	6	15
15.0%	2.250	9	6	15

Commercial polypropylene (PP) sorbent (New Pig, USA) used to compare the contact angle, buoyancy and oil sorption capacity with electrospun CA nanofibrous mats. A spin coated CA

film also compared in contact angle test. And this spin-coated CA films were prepared by using a two-stage spin coating (Spin Coater KW-4A, Chemat Technology) technique at steps of 600/2,500 rpm for 5 and 10 s for evenly spreading the 15% concentration CA solution.

2.2 High Throughput Electrospinning

A novel high-throughput electrospinning invented and modified by our former group member was used to produce CA nanofibers, its setup is shown in Figure 6(a). The whole set-up was made out of aluminum. Figure 6(b) and (c) showed the multi-jet disk which is the key part for high throughput. The metallic source disk has a height of 6 mm, the outer diameter was 10 cm, the depth was 2mm, and the inner diameter was 90 mm. There are 24 equidistant tubes drilled from the inside edge of the disk to the bottom of the disk with an angle of 45 degrees and one of them was. The diameter of these tubes is $\frac{1}{2}$ mm. Fluid solutions were pumped into the hollow source disk from a 10ml syringe through a kind of plastic tube with the help of a programmable syringe pump (Kd scientific).

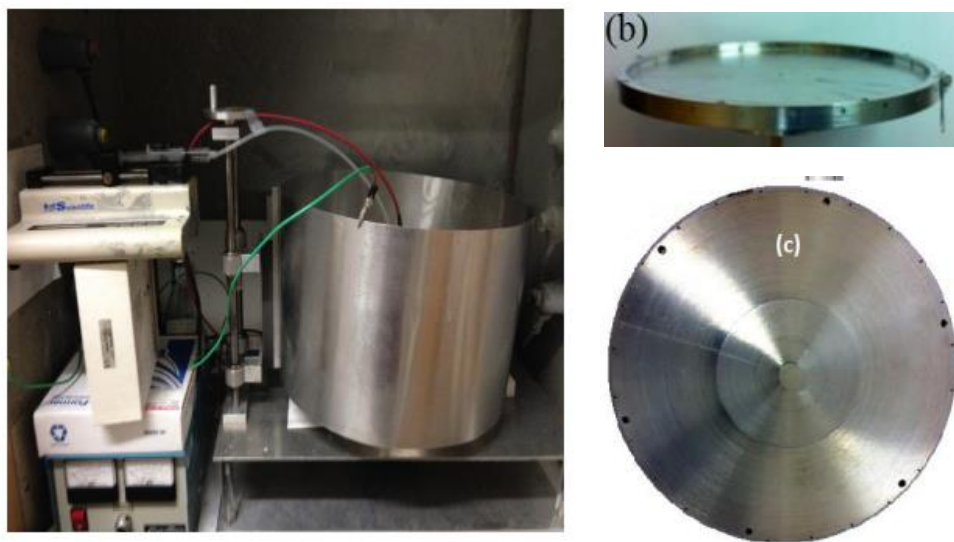
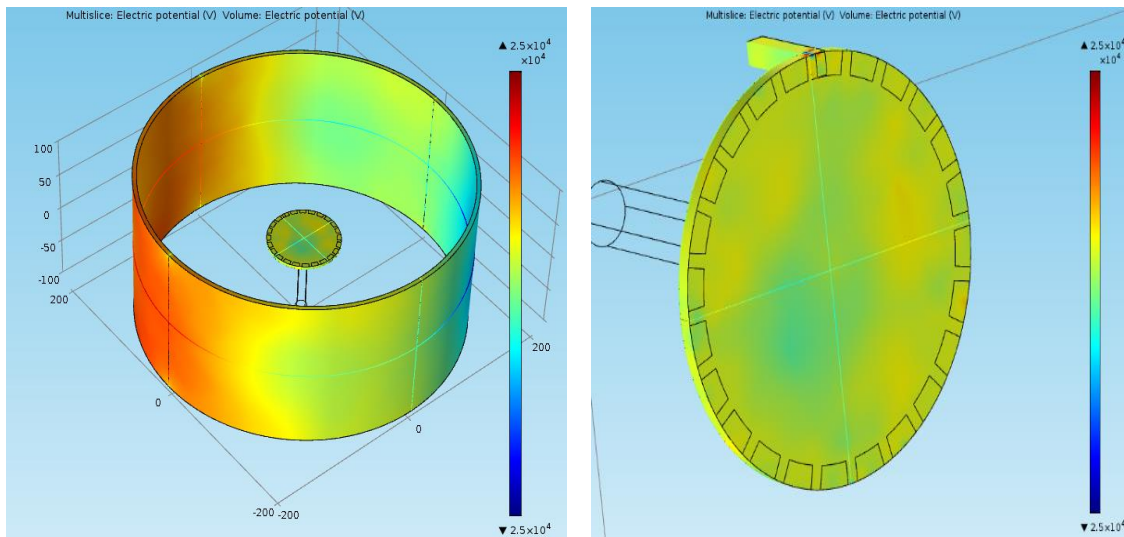


Figure 6: (a) Schematic of the high throughput set up (b) The bottom view of the source disk (c) The top view of the source disk

The flow rate was kept at a relative higher value, about 10 or more times higher than the traditional needle electrospinning. The value is 25 ml/hr in our experiment process. The working distance was kept at 15cm, which was the difference between the outer collector cylinder and the source disk. The collector is covered with aluminum foil, and Teflon was sprayed onto it to help get smoother fiber and made it easier to tear up fibers after electrospinning.

A Gamma High Voltage Research DC Voltmeter was used to supply a high voltage. The red electrode was connected to the edge of the disk to provide high voltage and the green one was connected to the collector and ground. The electric field distribution around the collector and spinneret surface has been studied by our former group member ^[49]. As showed in figure 7(a) around the collector the side near the electrodes connect point has the highest intensity electric field which result in a higher yield of fiber formation on this side. On the disk bottom, it has a uniform electric field distribution figure 7(b).



(b)

Figure 7: The electric field distribution around the (a) collector and (b) spinneret surface ^[49]

The whole setup was put into a fume hood to avoid harmful scent came out. Figure 8 showed the working condition of the high throughput set up. It was perfect as nearly all holes worked.



Figure 8: The view of high throughput electrospinning working condition

The production rate of nanofibers was calculated after the high throughput electrospinning. Measuring the duration of the run, and finding out the weight of the aluminum foil before electrospinning and after, and calculating their ratio, gave us the fabrication rate in grams per hour (g/h).

2.3. Characterization

Scanning electron microscopy (SEM) is employed to observe the morphology of the nanofibers after high throughput electrospinning. In order to ensure conductivity and reducing charging effects on the surface, an appropriate size fiber sample needs to be prepared with

conductive materials coating (figure. 9). During the SEM test, the electrons will interact with the atoms on the surface of sample, providing various signals for the electromagnetic lenses to detect, so the sample's surface morphology can be received^[50]. According the SEM images we can see how the fibers like, whether the beads exist, the diameter size of fibers, etc.

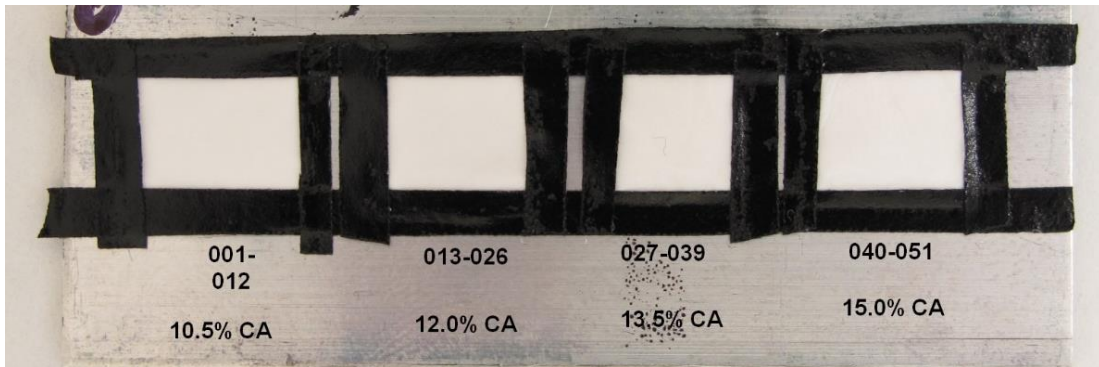


Figure 9: SEM sample preparation for 4 different concentration CA nanofibrous mats

2.4. Contact Angle Test

The water contact angle were measured by optical contact angle meter (CAM 200, KSV Instruments Ltd) to see the degree of hydrophobicity for fibers.

When a droplet dropped on either solid or liquid surfaces, it will spread to minimize its total surface energy^[51]. Consider a simplified model as showed in Figure 10^[52]. Assume the solid phase is smooth, planar, non-porous, and uniform in composition. And the test liquid is assumed to be a pure compound. At point P, there are three forces that act on the droplet. These forces are represented by the arrows in the Figure, where γ_{SA} is the interfacial tension between the solid and air, γ_{SL} is the interfacial tension between the solid and liquid, γ_{LA} is the interfacial tension between the liquid and the air. At equilibrium the three vector quantities sum to zero and they

form a contact angle, θ , which is the angle tangent to the liquid surface makes with the solid surface.

According to the Young equation [53], at equilibrium:

$$\gamma_{SA} = \gamma_{LS} + \gamma_{LA} \cos \theta \quad (1)$$

$$\cos \theta = (\gamma_{SA} - \gamma_{LS}) / \gamma_{LA} \quad (2)$$

$$\theta = \arccos(\gamma_{SA} - \gamma_{LS}) / \gamma_{LA} \quad (3)$$

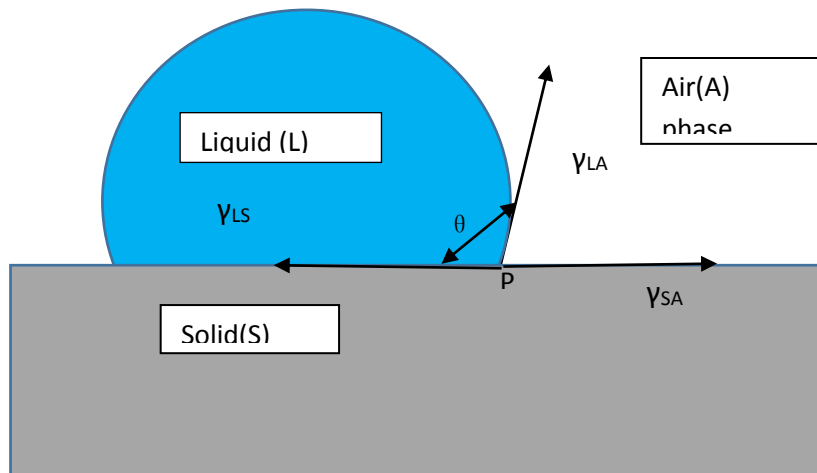


Figure 10: Definitions of terms in Young’s equation, describing the balance of interfacial tensions in the plane of the surface when a droplet of oil is placed on a solid “S” in the presence of air (A)

Therefore, the degree of contact angle represents the surface forces between a liquid and a surface. In other words, the contact angle can determine the surface properties of specific materials to different liquid.

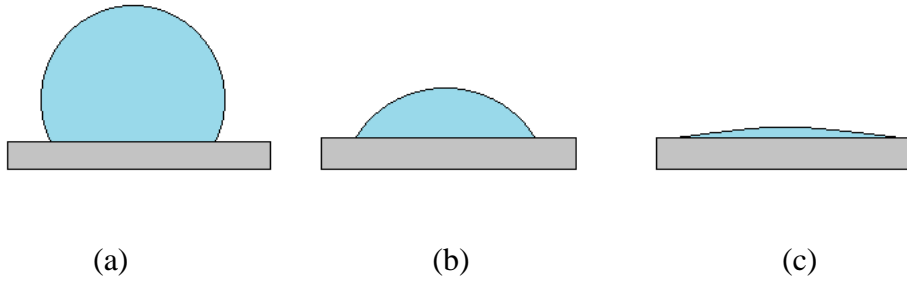


Figure 11: A drop of deionized water onto different surfaces

In generally, if the contact angle is greater than 90° , the fluid will resist spreading, and the surface is defined as “non-wettable” by the fluid (figure. 11(a)). By contrast, if the contact angle is less than 90° , the surface will be considered “wetable” (figure.11(b)). And if the contact angle close to 0° means the liquid is strongly attracted to the solid surface (figure.11(c)). If the liquid is water we can estimate is the material is hydrophilic or hydrophobic, as showed in figure 12^[54].

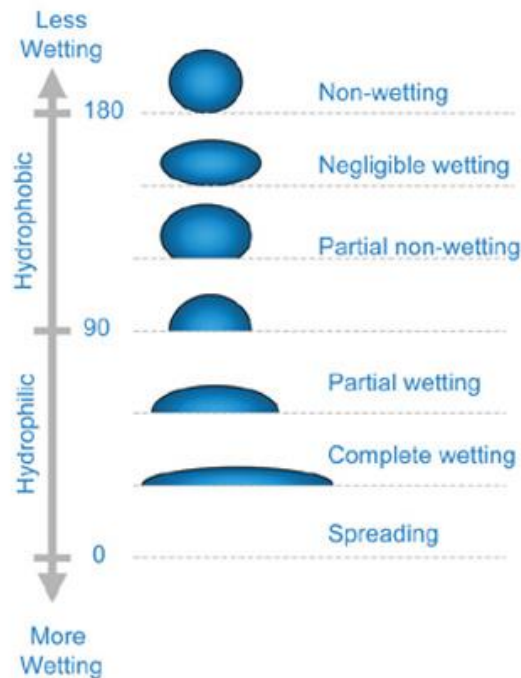


Figure 12: Hydrophobic and Hydrophilic properties related to contact angle ^[54]

To test the surface properties to the high throughput electrospun fibers we load the sample onto the stage of the optical contact angle meter and drop 5 μl deionized water onto the surface of the sample. Then use program 'KSV CAM 200' to calculate the water contact angle of the sample. In this test also used a commercial PP sorbent sample and a spin coating CA sample as the control group.

2.5 Oil Absorption Test

To measure the oil sorption capacity of CA fibrous, a standard of American Society for Testing and Materials (ASTM) 23 F726-99 ^[55] was used in this test. No.6 oil which is a type of commonly used oil was employed to proceed the oil absorption test. And the commercial polypropylene (PP) sorbent as control group also used in this test to compare the oil uptake ability to CA fiber mats.

According the classification for oil type and sorbent type in the standard which showed in table.7 and table. 8, the particulate sorbent is classified as type I sorbent and No. 6 oil is classified as a heavy oil.

Table 7: Classification of Oil types

Oil Type	Viscosity Range	Density Range
Light	1-10 cP	0.820-0.870 g/cm ³
Medium	200-400 cP	0.860-0.930 g/cm ³
Heavy	1,500-2,500 cP	0.930-1.000 g/cm ³
Weathered	8,000-10,000 cP	0.930-1.000 g/cm ³

Table 8: Classification of Sorbent Types

Sorbent Type	Description
Type I	A material with length and width much greater than thickness and which has linear form and strength sufficient to be handled either saturated or unsaturated
Type II	An unconsolidated, particulate material without sufficient form and strength to be handled except with scoops and similar equipment
Type III	Absorbent material contained by an outer fabric or netting which has permeability to oil, but with openings sufficiently small so as to substantially retain the sorbent material within the fabric or netting.
Type IV	An assemblage of standards, open netting, or other physical forms giving an open structure which minimally impedes the intrusion into itself of high viscosity oils.

Both a short test (15 minutes) and long test (24 hours) were operated in this test. First sample pieces of sorbents were cut into squares (13 by 13 cm) then weighed as showed in figure 13 recorded as W_1 . Then the sorbent sample is placed into a stagnant test cell

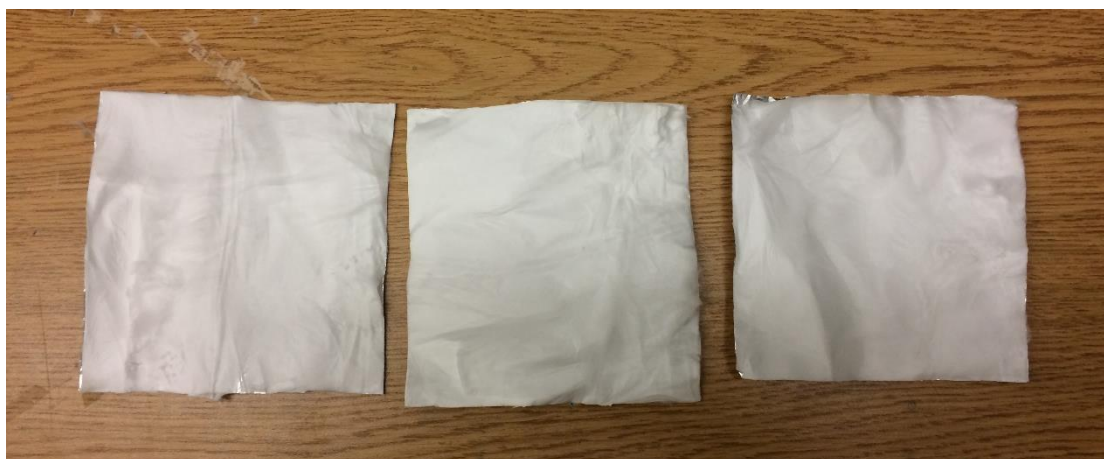


Figure 13: 13 by 13 cm square samples for oil sorption test

which is filled with a layer of test liquid with a depth of approximately 80 mm. Wait 15 minutes \pm 20 seconds for short test and 24 hours \pm 30 minutes for the long test and remove the sample from the cell and allowed to drain for 2 minutes. After that immediately place a weighing pan which has been weighed as W_p under the sample to catch additional drips and transfer the sample to the pan then recode the weight as W_2 . All tests were performed at a room ambient and conducted in triplicate.

The oil-absorbency, Q , was calculated by following equation:

$$Q = \frac{W_2 - W_p - W_1}{W_1}$$

2.6 Buoyancy Test

The buoyancy ability of the sorbent is important for collecting after oil clean-up use and not bring new pollution into the environment.

To test how long it can stay on the water, a buoyancy test is performed. As showed in figure 14, in order to distinguish, 4 concentration CA fiber mats were prepared with different shapes. Then put these sample in a crystallizing dish with half-dish water like showed in figure 15. A compare group of commercial PP sample also employed in this test. All the samples stay on the water. Record their conditions every week.

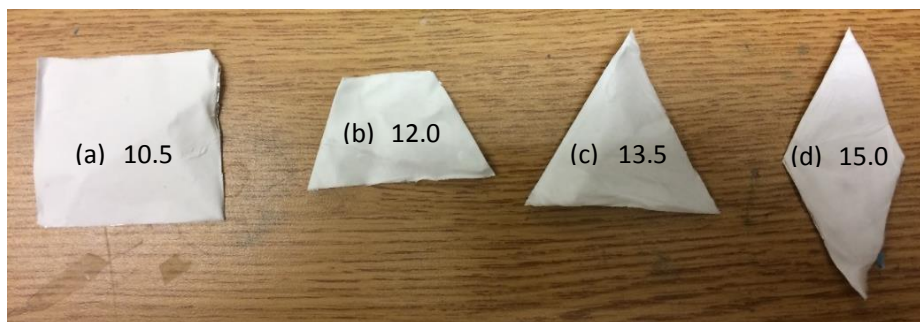
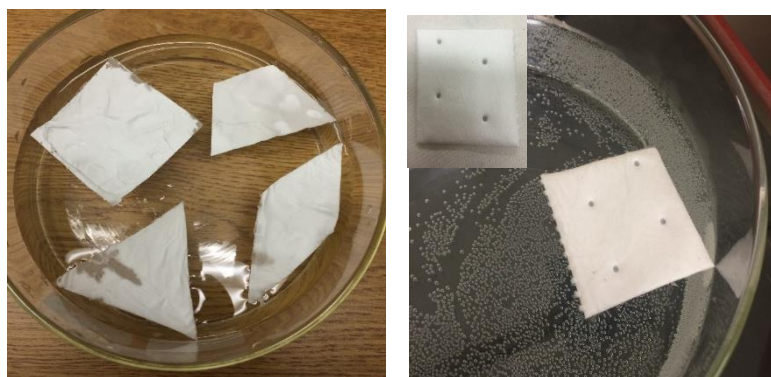


Figure 14: CA nanomats samples for buoyancy test: (a) 10.5% CA (b) 12.0% (c) 13.5% (d) 15.0%



(a)

(b)

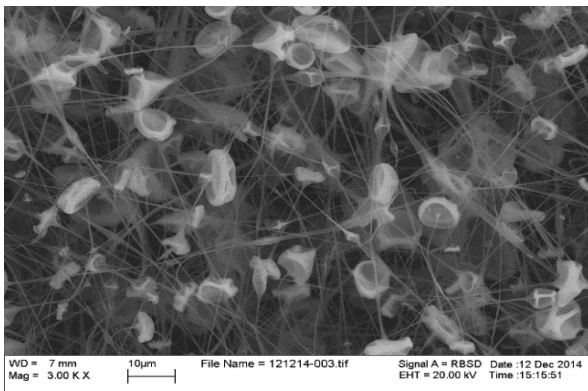
Figure 15: First-day view for buoyancy test: (a) electrospun nanofibrous mats (b) commercial PP

Another test was conducted by putting a piece of 15% concentrated CA sample into an oil-water bath to see its buoyancy after saturated oil.

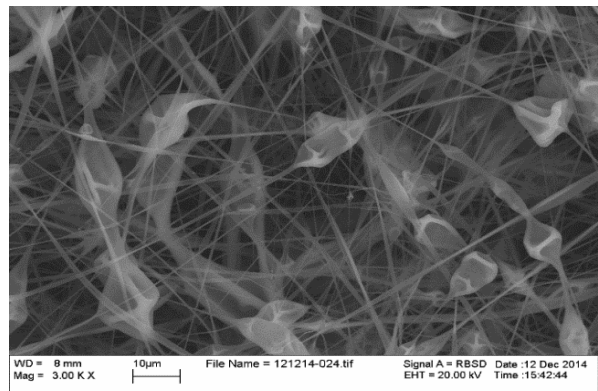
Chapter 3: Results and Discussion

3.1 Materials Characterization Results and Discussion

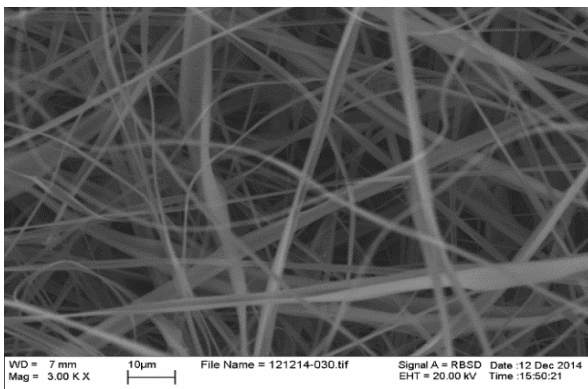
Figure 16 compared the 4 different concentration CA SEM results at a magnification of 10 μ m. A mixture of beads and fibers is obtained at the concentration of 10.5%. With the increase of the concentration, the shape of the beads changes from spherical to spindle-like at 12.0% concentration and in 13.5% the beads disappear and mostly uniform fibers with a few ribbon-like fibers were observed. When the concentration increased to 15.0%, a few spindle-like beads showed again but the fiber amounts still occupied in the main phase.



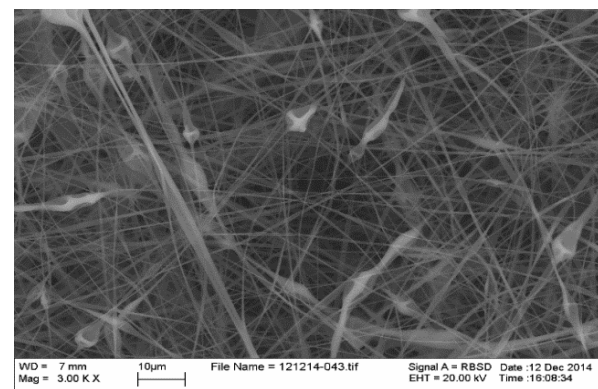
(a) 10.5%



(b) 12.0%



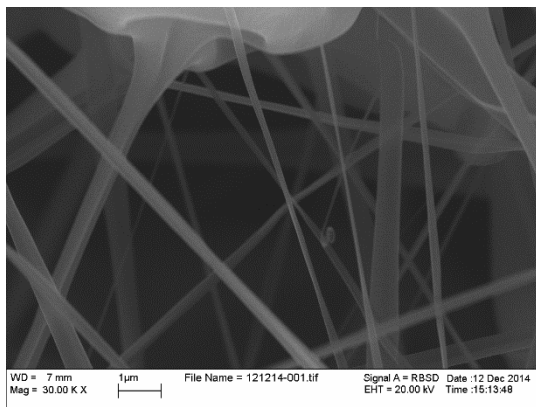
(c) 13.5%



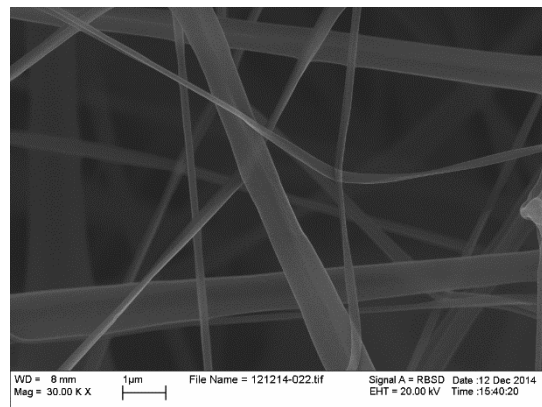
(d) 15.0%

Figure 16: SEM images of 4 different concentration CA nanomats at a 10 μ m magnification: (a)10.5% (b)12.0% (c) 13.5% (d) 15.0%

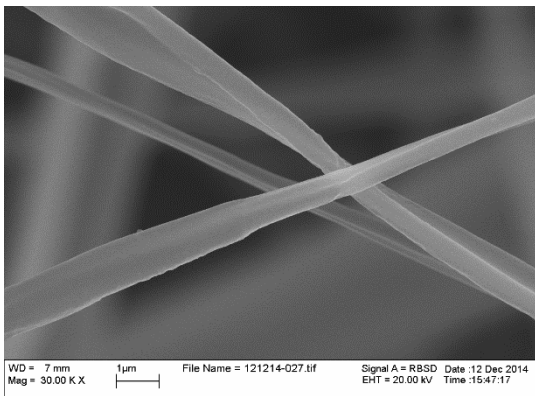
The figure 17 compared the 4 different concentration CA SEM results at a magnification of $1\mu\text{m}$. We can see the trend of diameter size change in these figures. With the concentration increased from 10.5% to 13.5% the diameter size of fiber also increased. And with a concentration of 15% the fiber diameter size decreased. Table 9 and figure 18 showed the influence of the concentration on the diameter of CA fibers. And the production rate of high throughput electrospinning increased in a remarkable scale compare with traditional eletrospinning.



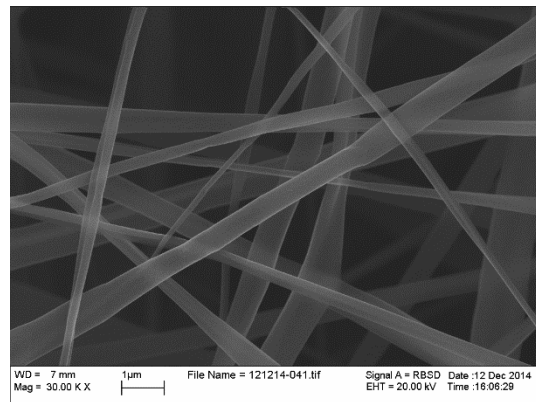
(a) 10.5%



(b) 12.0%



(c) 13.5%



(d) 15.0%

Figure 17: SEM images of 4 different concentration CA nanomats at a $1\mu\text{m}$ magnification: (a)10.5% (b)12.0% (c) 13.5% (d) 15.0%

Table 9: Effect of concentration on CA fibers under same voltage, working distance and flow rate

Concentration(g/lm)	Voltage(kV)	Distance(cm)	Flow rate (ml/hr)	Production(g/h)	Diameter(nm)
10.5%	24	15	25	1.36	145
12.0%	24	15	25	2.37	672
13.5%	24	15	25	2.73	1084
15.0%	24	15	25	3.03	475

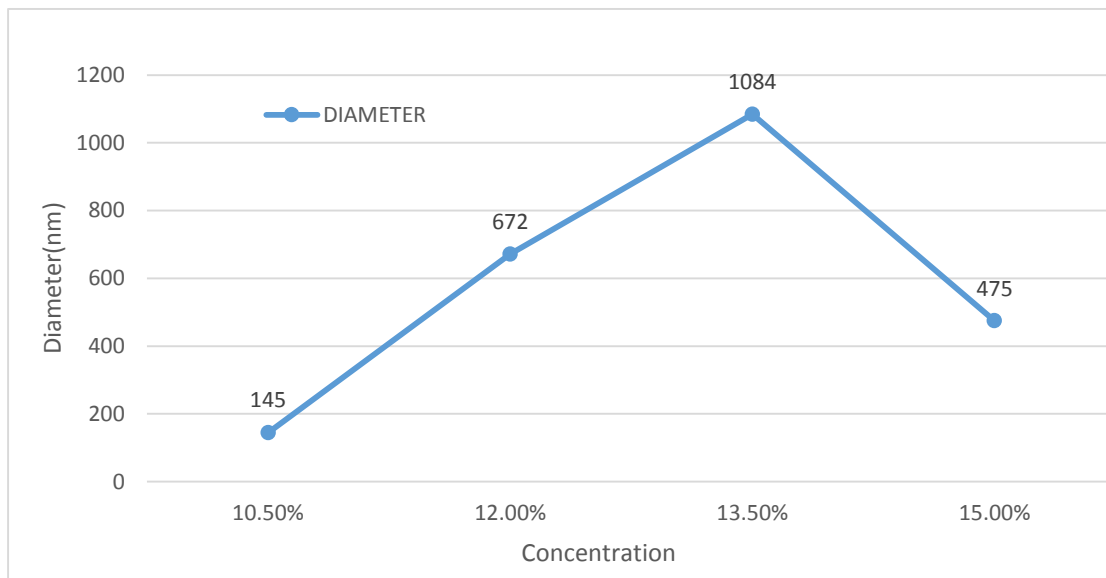


Figure 18: Plot of diameter vs. concentration

In the high throughput electrospinning process the working distance, flow rate, and applied voltage were all kept in a same and appropriate number for the 4 different concentration CA precursors. The concentration determined the viscosity of the solution which is important for fiber forming. A lot of studies ^[37] showed that with very low viscosity there is no continuous

fiber formation and with very high viscosity there is difficulty in the ejection of jets from the solution, which is same with our result.

Specific surface area "SSA" is determined by the diameter size of the fiber. According the chart the diameter size increased with the increasing of concentration from 10.5% to 13.5% and decreased at 15%. However to consider the presence of the beads the SSA for the whole CA mats may different with this fiber diameter size-related trend. Since the beads have a weak SSA, the number of the beads in the whole CA mats may reduce its SSA. Thus among these 4 CA fiber mats the 15% concentration one with a small diameter, and just a few ribbon-like beads may has the highest SSA.

There should be an optimum solution concentration for the electrospinning process that can get a uniform fibers with a smallest diameter. In this case, it should be between 13.5% and 15%.

3.2 Contact Angle Test Result and Discussion

Figure 19 shows the results of the contact angle test for the 4 different concentration CA fiber mats. All of the 4 fiber mats has a high water contact angle around 130° (130.36° for 10.5% CA, 129.03° for 12.0% CA, 128.38° for 13.5% CA and 128.95° for 15% CA) which indicate a high hydrophobic ability.

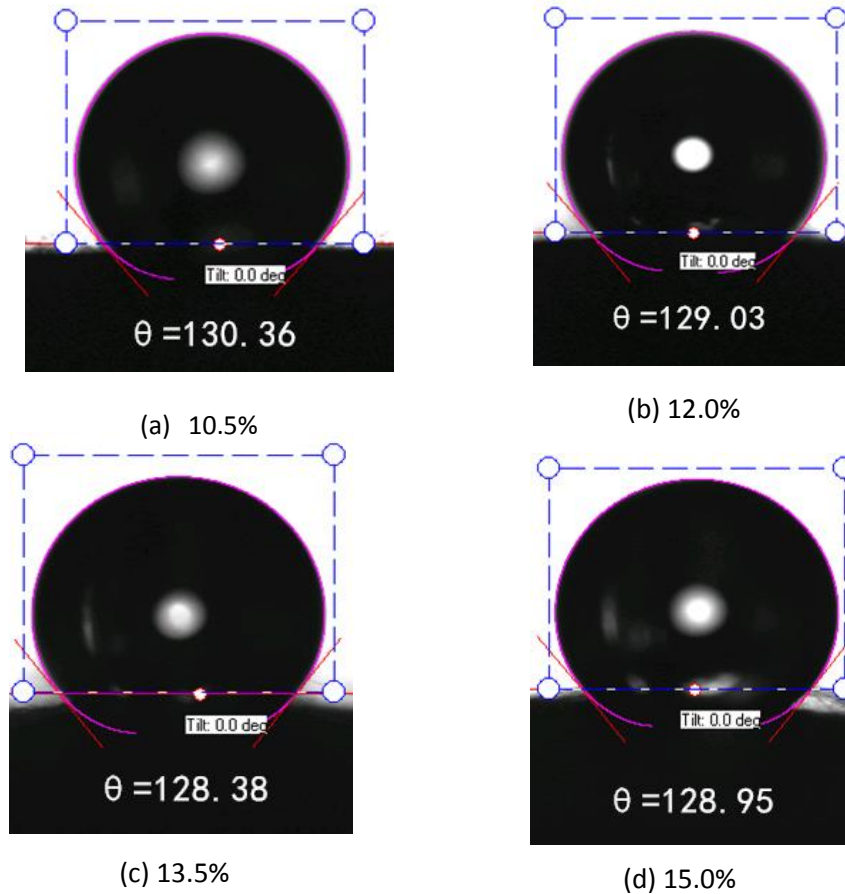
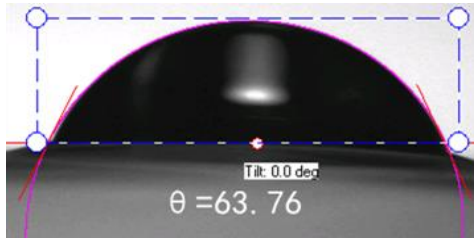
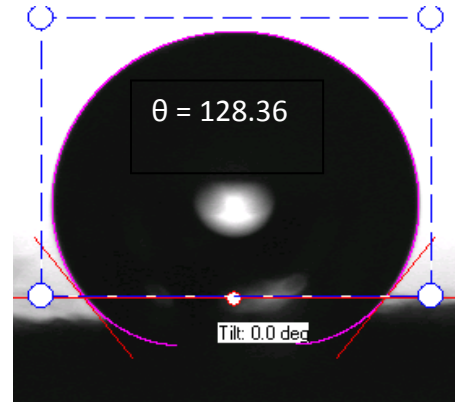


Figure 19: Water contact angle results for 4 different concentration nanomats: (a) 10.5% CA (b) 12.0% CA (c) 13.5% CA (d) 15.0% CA

Figure 20 shows the results of a contact angle test for a spin-coated CA thin film prepared from a same solution of 15% concentration, and a commercial PP sorbent. The spin-coated CA film prepared by the same 15% concentration CA solution, Figure 20 (a), shows a lower contact angle of 63.76° , indicating hydrophilic. And in figure 20 (b), commercial PP sorbent sample shows a contact angle of 128.36° which is almost same with my CA mats sample indicating hydrophobic.



(a) Spin-coated CA film



(b) Commercial PP

Figure 20: Water contact angle results for (a) Spin-coated CA film (b) Commercial PP

Also the contact angle for oil test has been tried on the 4 different concentration CA mats sample, but the oil droplet will immediately spreading on the surface, that is to say, the oil contact angle is approximate to zero.

The contact angle is determined by surface tension according the Young equation [53] below:

$$\cos\theta = (\gamma_{SA} - \gamma_{LS}) / \gamma_{LA}$$

Thus, if $\theta < 90^\circ$ means the $\gamma_{SA} > \gamma_{LS}$ while $\theta > 90^\circ$ means the $\gamma_{SA} < \gamma_{LS}$. In this case for electrospun CA fiber mats the interfacial tension between the water droplet surface and mats surface is bigger than the interfacial tension between the air and mats surface. However, the CA mats surface is rough and with a lot of porous formed by folded random fibers on it. Thus, the real situation is more complicated which need to do deep research.

According to the opposite contact angle test result between electrospun CA fiber and spin-coated CA film, it can be proved the structure has an important effects on surface property. The hydrophobic surface made CA fibrous mats a desirable property of oil/water selectivity as sorbent.

3.3 Oil Sorption Test Result and Discussion

Table 10 listed the contents of oil sorption short test for 4 different concentration CA fiber mats and Commercial PP. Each group is conducted in triplicate within a same environment and then calculate the average oil sorption ability. The sorption capacity of CA fibrous mats and commercial PP sorbent for No. 6 fuel oil are 10.2926 (10.5% CA), 12.0402 (12.0% CA), 21.1836 (13.5% CA), 29.7572 (15% CA) and 7.1587 g/g respectively in the short test. The sorption capacity of the CA fibrous mats increased with the increasing of precursor concentration. All of the 4 kinds of CA fibrous mats have a higher oil sorption capacity than commercial PP sorbent as showed in figure 21.

Table 10: The contents of short oil sorption test (15 Minutes)

	10.5% CA			12% CA			13.5% CA			15% CA			Commercial PP		
Sample	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Temperature(F)	67			71			70			70			70		
Humidity	10%			9%			9%			9%			9%		
Sample weight(g)	0.49	0.47	0.42	0.33	0.28	0.74	0.36	0.36	0.46	0.50	0.53	0.61	6.64	5.91	6.61
Initial Capacity(g _{liquid} /g _{sorbent})	9.98	10.35	10.54	12.49	12.31	11.33	20.36	20.88	22.30	30.15	30.87	28.2	7.21	7.50	6.76

Average Liquid uptake($g_{\text{liquid}}/g_{\text{sorbent}}$)	10.29	12.04	21.18	29.76	7.16
Standard Deviation($g_{\text{liquid}}/g_{\text{sorbent}}$)	0.13	0.25	0.31	0.35	0.20

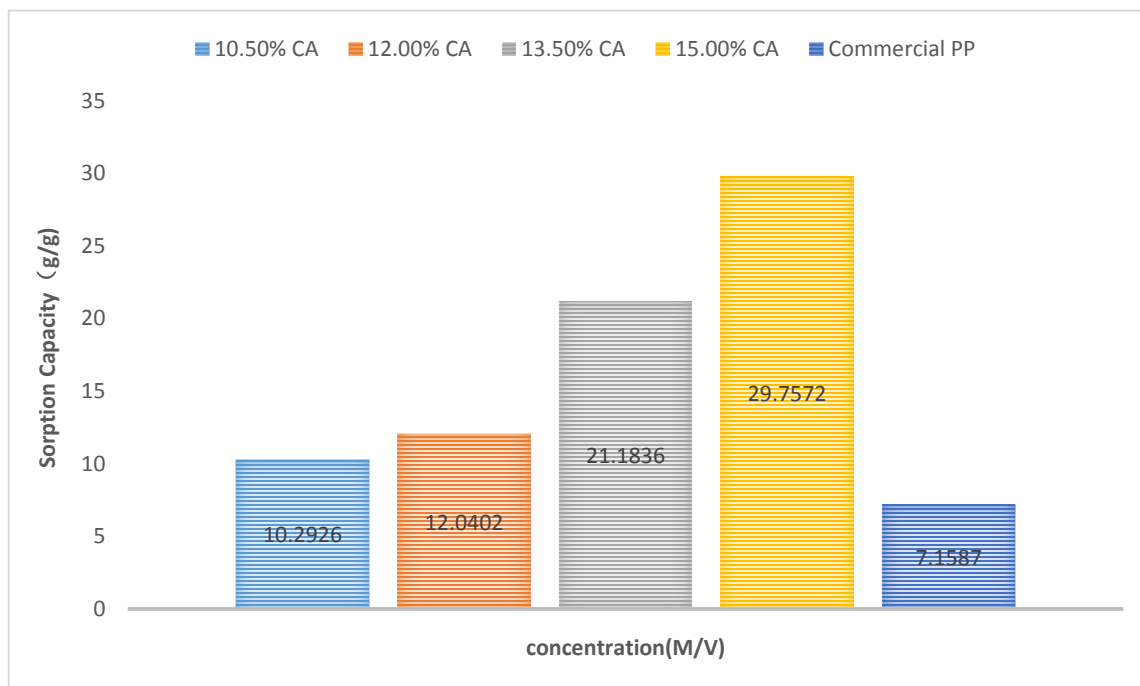


Figure 21: The oil sorption capacity in short test for 4 different concentration CA and commercial PP

As showed in table 11 the sorption capacity of CA fibrous mats and commercial PP sorbent for No. 6 fuel oil are 11.7026 (10.5% CA), 14.5101 (12.0% CA), 22.4119 (13.5% CA), 31.6792 (15% CA) and 8.6569 g/g respectively in the long test, which bigger than in short test. Similarly, all of the 4 kinds of CA fibrous mats have a higher oil sorption capacity than commercial PP sorbent as showed in figure 22.

Table 11: The contents of long test for oil sorption (24 Hours)

	10.5% CA			12% CA			13.5% CA			15% CA			Commercial PP		
Sample	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Temperature(F)	67			68			67			70			70		
Humidity	10%			10%			10%			9%			9%		
Sample weight(g)	0.41	0.42	0.61	0.51	0.63	0.49	0.37	0.29	0.37	0.68	0.52	0.57	6.58	6.80	6.87
Initial Capacity($\frac{g_{liquid}}{g_{sorbent}}$)	11.71	12.17	11.22	14.65	14.47	14.41	21.91	23.36	21.96	30.95	32.44	31.65	8.82	8.59	8.56
Average Liquid uptake($\frac{g_{liquid}}{g_{sorbent}}$)	11.70			14.51			22.41			31.68			8.66		
Standard Deviation($\frac{g_{liquid}}{g_{sorbent}}$)	0.20			0.05			0.25			0.19			0.07		

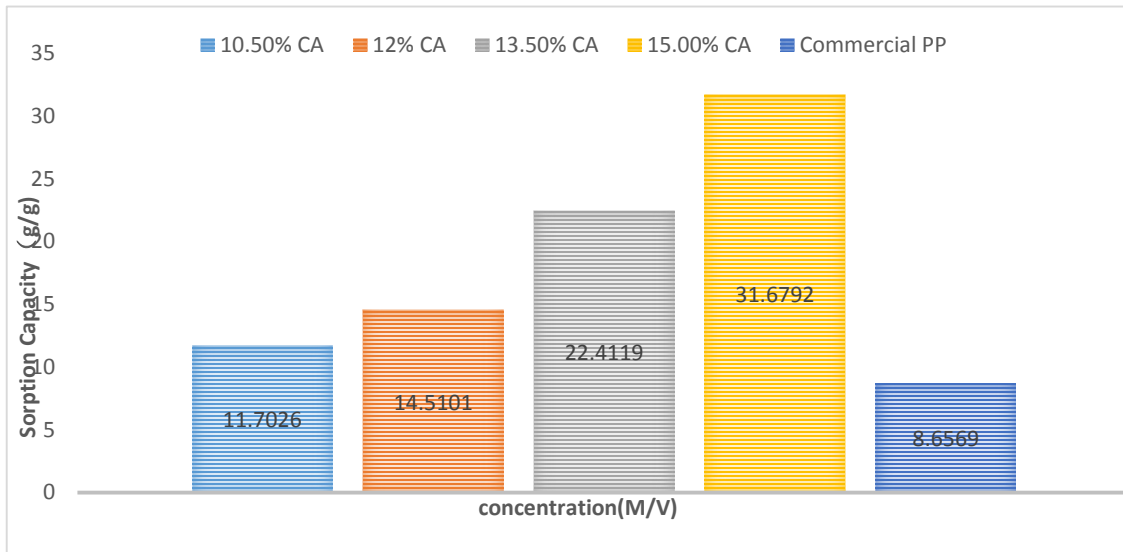


Figure 22: The oil sorption capacity in long test for 4 different concentration CA and commercial PP

In former contact angle test, the electrospun CA fibrous mats showed a good oleophilic property. In my guess, the oil sorption ability may be effected by its structure. According the SEM results, the beads number is very small in 13.5% and 15% CA fibrous mats. The folded fibers formed a lot of tubes and pores interiors which provide more space to catch the oil. The size of these tubes and pores also important, too big size may result in oil run away from the sorbent. And small size tube and pores may have capillary action which also good for oil up-taken ability for sorbent. Beads numbers are large in 10.5% and 12.0% CA fibrous mats which result in a lot of big empty space between these beads and oil may run away from these large space. Maybe this is why 10.5% and 12.0% CA fibrous mats have a much lower oil sorption ability than 13.5% and 15.0% ones.

3.4 Buoyancy Test Result and Discussion

As showed in figure 23, after 17 weeks all the 4 kinds sample still stayed on the water surface, which indicate a good buoyancy ability on the water. Compare with the first day of this test, all these samples still keep their original shapes, no loose and breakdown observed. Only the whole body of them were wetted by water may be because of it only has submicron sized thickness. The control group commercial PP sample also showed a good buoyancy ability after 10 weeks as showed in figure 24. The commercial PP product is 2 micron thick and is made up of several layers PP mats with an enclosed cover to which may result an improvement on its buoyancy and mechanical properties. However, it still cannot tell which one has a better buoyancy property until the sink day recorded.

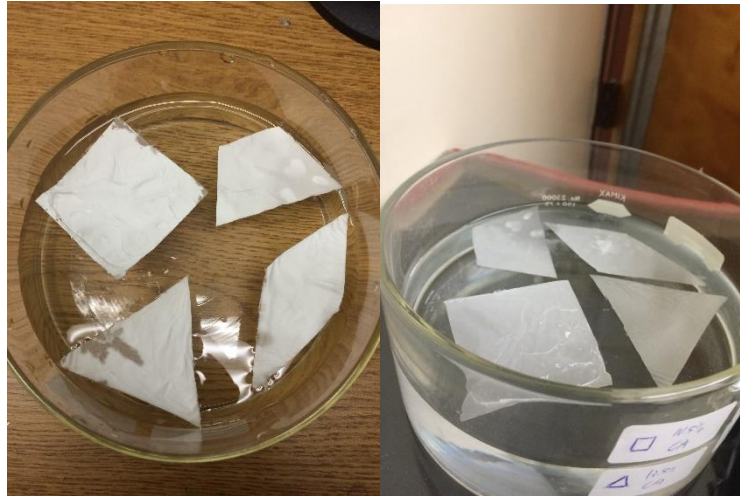


Figure 23: (a) First-day view of 4 different concentration CA nanofibrous mats in buoyancy test (b) After 17 weeks later the view of 4 different concentration CA nanofibrous mats in buoyancy test



Figure 24: (a) First-day view of commercial PP in buoyancy test (b) After 10 weeks later the view of commercial PP in buoyancy test

Figure 25 showed the buoyancy test result in the water-oil bath for 15% CA fibrous sample. A layer of No. 6 fuel oil is removed by addition of the CA fibrous mats and the sorbent was stayed on the top of the water.

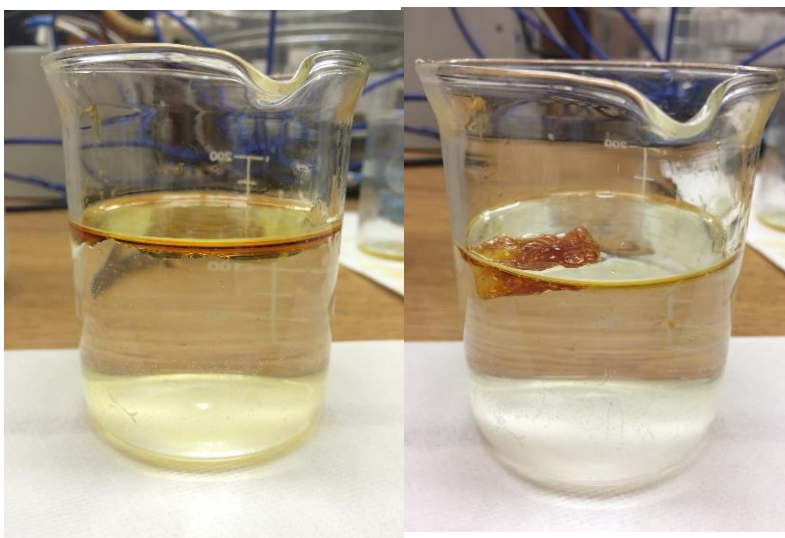


Figure 24: Buoyancy result for 15% CA mats in water-oil bath

Buoyancy is also an important property for oil sorbent in practical use. Buoyancy is closely related to density and pore volume of the materials^[27]. In the former test, it has been proved that electrospun CA fibrous mats have an ability of hydrophobic. And its structure with a large number of the pore volume may result in its good buoyancy.

3.5 Comparison Between Electrospun CA Mat and Commercial Sorbent.

Generally speaking, polypropylene (PP) is the most common used materials for commercial sorbent.

Both CA and PP have the same advantages of biodegradable and cheap. However, in this study CA showed many times higher oil capacity than commercial PP at a fraction of PP thickness and weight. Also, a high throughput device was used in this study to prepare CA mat, which made a possible way for the manufacturing of CA mat. The buoyancy property

comparison still need to see since both electrospun CA mat and commercial PP sorbent has not sink yet.

After all, electrospun CA mats can be a perfect substitution for PP as commercial sorbent.

Chapter 4: Conclusion and Future Work

A series of non-woven nanofibrous mats with a 3D fibrous structure were successfully prepared from 4 different concentration precursor 10.5%, 12.0%, 13.5% and 15.05 w/v CA/ acetic acid-acetone solution by using a novel high-throughput electrospinning device. All of them showed a hydrophobic surface properties with a water contact angle of 130°. A good buoyancy property on the water of these nanofibrous mats was also observed either for dry-nanofibrous mats or oil-saturated nanofibrous mats. An oil sorption test has been conducted under a guidance of ASTM standard. All of these 4 nanofibrous mats showed a better oil sorption capacity than commercial PP sorbent and 15% CA mats even has a 4 times better oil uptake ability than commercial PP sorbent. In addition, the CA fibrous mats are biodegradable and will not cause supplementary pollution. Therefore, electrospun CA nanofibrous mats is a good candidate as oil sorbent for oil spill cleanup use.

Since the marine environment is very complicated for its high salinity and the unstable surface etc., the properties of CA nanofibrous mats may be affected by these factors. Future research should be done to establish a maritime virtual environment for the test. The eletrospinning process also requires deep-going research to prepare best fibrous nanofiber. In addition, to make the CA nanofibrous mats become a good sorbent product, the product design should be done such as the commercial PP sorbent which made up of several layers PP mats with an enclosed cover to improve its mechanical properties.

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