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PVP-CA composite preparation and its characteristics

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Abstract of the Thesis

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Polyvinylpyrrolidone (PVP) is a commonly used polymer that has some excellent properties, such as great strength and biocompatibility. Cellulose Acetate (CA) is another excellent polymer that has been employed in many applications, including drug. PVP-CA composite has both strength and flexible properties that can be used as ultrafiltration membranes or the drug release system.

PVP-CA composites comprise a new class of materials that have been the scope of this work. In this research, the electrospun PVP-CA composites were prepared under different concentrations. Then, the impact of different electrospinning parameters on fiber diameters was investigated. Moreover, acetic acid and acetone were used as solvents for dissolving PVP, CA respectively. For comparison, PVP in water and CA in acetone was each deposited on the aluminum foil by electrospinning, forming a two-layer structure.

Scanning electron microscopy(SEM) and Raman spectroscopy test were carried out. From the test results, fibers with 200nm to 1um diameter were prepared and the interaction between PVP and CA were proved.

Then the oil absorption testing was carried out. The membrane structure of the electrospun composite fibers showed good oil absorption capacity, that was twice higher than the 2-layer PVP-CA fibers.

Dedication Page

Dedicated to my beloved parents

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CHAPTER 1: INTRODUCTION

1.1 Polyvinylpyrrolidone (PVP)

Polyvinylpyrrolidone(PVP), in this thesis, it is referred simply as PVP. Which is the general name of the water soluble homopolymer – N-vinyl-2-pyrrolidone(NVP). This kind of polymer is an important polymer that has many excellent properties. PVP was first developed in Germany at I.G. Farben by Professor Walter Reppe and his colleagues in 1930s. At that time, PVP was widely used in the blood system, the Blood Plasma Expander[1]. This application helped a lot patients in the 1930s and 1940s. Since PVP has some advantages for this application, like the nonantigenic, no cross-matching, non toxic and carries no dangers for the infection, thus started the biomedical application of the PVP material.

PVP is readily prepared by polymerization of N-vinyl-2-pyrrolidone (NVP). And the NVP is produced by the reaction of acetylene and formaldehyde. The PVP fabrication reactions are based on the Reppe acetylene chemistry[4].

The following series of reactions are the Reppe synthesis of PVP:

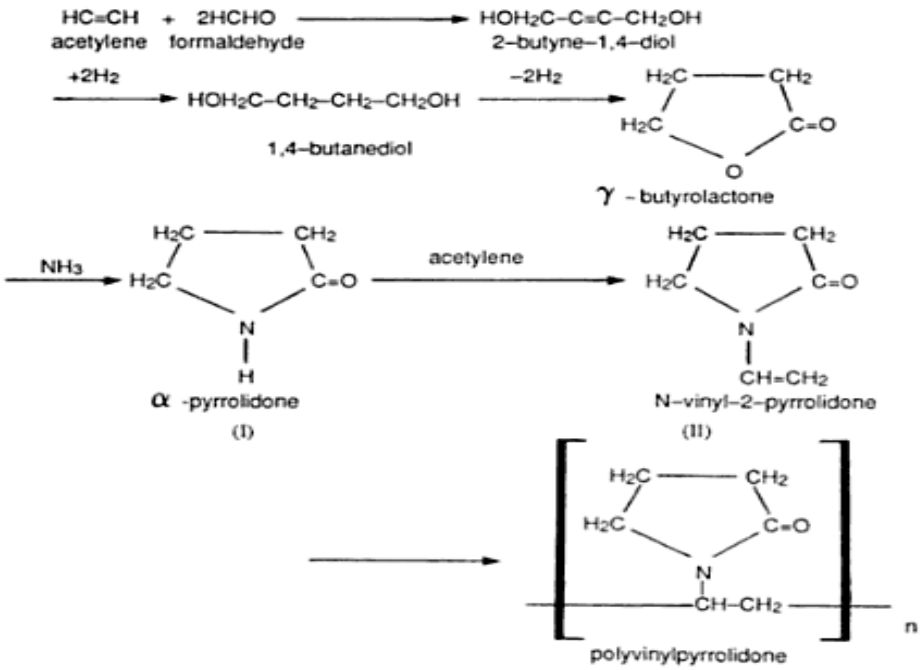


Figure 1: Reppe synthesis of PVP*(B.V. Robinson, PVP: A Critical Review of the Kinetics and Toxicology of Polyvinyloyrrolidone,1990)*

1.1.1 Properties and Applications

PVP has many excellent properties, such as solubility in variety of organic solvents, biological compatibility, low toxicity, film-forming, adhesive characteristics, inert to chemical modification and resistance to thermal degradation[4].

Due to above mentioned properties of PVP, in can be used in vatious applications. PVP is soluble in many kinds of organic solvents, such as alcohols(ethanol), acids(acetic acid), Esters(Ethyl Lactate), Ketones(Methylcyclohexanone), Amines(Triethanolamine) and so on. However, it does not dissolve in ketones(Acetone), Esters(Diethylether), Ethers(Diethylether) and Hydrocarbons. Most importantly, water is a good solvent for PVP since PVP has some hydrophilic groups.

Biomedical applications

PVP is a bio-compatible and homogeneous polymer with very low toxicity and solubility in water. So materials coated by or combined with this polymer can be used as medical devices intended for implanting in the human beings body, such as the template for drug delivery and drug capsules[2]. PVP won't stimulate the skin and mucous membrane. Recently, some PVP based polymer composites has been produced to improve the drug release time and release volume of medicines.[3]

Food fabrication

From the U.S. Food and Drug Administration (FDA), PVP has been approved for many uses as food additive, including a binder for vitamin concentration tablets and as an additive for synthetic sweetener tablets[4]. It can react with specific polyphenol compounds to form a complex material[4]. That's why it has been widely used in bear, wine and juice production as stabilizer and clarifying agent. Another usage of PVP is as the color stabilization of some beverage. What's more, PVP also can be used as food coatings and packaging materials, but only for dry food. If it contacts with wet food, like some fresh fruit, it may dissolve.

Cosmetic applications

Similar to its application in pharmacy, it has been widely used in the cosmetic field. It will never hurt the skin. PVP and its copolymers have good dispersion and film properties, thus can be used as a dispersing agent, binder and lubricant in the cosmetic industries. Generally, PVP can be used in the skin cleansing, facial lotion, hair setting lotion and for improving the consistency of shampoos.

Detergent

PVP has properties that can resist the deposition of dirt or the oil, so it can be used in the preparation of transparent liquid or heavy dirt detergents. By adding PVP into detergents, the cleaning ability can be improved[4]. Since PVP has lipophilicity groups, when it has been added into the detergent, the lipophilicity groups can react with oil then help to remove it.

Dyeing applications and inks

PVP improves the solubility of dyeing material to show great and more uniform color. And in the paper and fiber dyeing industry, it helps dye reception in the materials.

1.2 Cellulose Acetate (CA)

Cellulose Acetate is the ramification of cellulose. CA was first created in 1865 by Paul Schutzenberger. He used cellulose to react with acetic anhydride. Then, in 1904, cellulose acetate was discovered that it can dissolve in some solvent, like the acetone.

Cellulose is a natural polymer that can be found in plants. That's why CA attracts a lot of attention from the scientist. Since cellulose can be achieved from the natural plants, CA is really cheap and can be easily fabricated based on its abundant resource. Another reason that CA is widely used is its product characteristics.

Here is the chemical structure of cellulose and cellulose acetate:

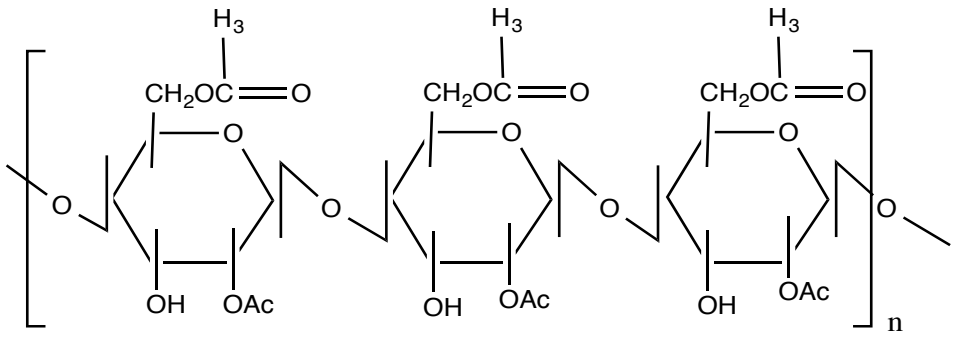


Figure 2: Molecular structure of cellulose acetate

For cellulose, the functional groups should be Hydroxyl groups. Hydroxyl groups connected with carbon to provide good properties. To produce CA from cellulose, the acetic anhydride and sulfuric acid are needed. At first, cellulose should be ice bathed to provide a cold condition to react with acetic anhydride and the sulfuric acid. When the reaction has occurred, two hydroxyl groups in cellulose are replaced by $OCOCH_3$ and one is replaced by OSO_3H. Secondly, to remove the irrelevant OSO_3H group, acetic acid added to the reaction reagent after that. After the new reaction between the acetic acid and the intermediate, the OSO_3H is removed and the cellulose acetate will be produced.

1.2.1 Properties and applications

CA is not a water soluble polymer because it is nonpolar material that requires organic solvents to from stable dispersion. It is water soluble only when other organic solvents are used in conjunction. The commonly used solvents for CA are acetone and acetic acid.

CA has many applications. It was firstly used in photography and some coatings as a component. Without these, CA can be prepared as film, negative component in camera for motion pictures or the computer tape. Until now, much researches have been done to CA

fabrication and applications, like the paper and wood products, pharmaceuticals, biomedical fields, textile chemistry, plastics fabrication and usage and the coating materials[5]. In recent years, CA showed excellent characteristics, like its biocompatible and biodegradable material which can be used in biomedical applications. CA is film- and fiber-forming materials, scientists often use electrospinning technique to fabricate it. CA fibers can be used in biofunctionalization (drug delivery and tissue engineering), bioremediation, antimicrobial mat, self-cleaning textile, thermoadapatable material, photochromic device application, biosensor and anti-counterfeiting material, nutraceutical delivery system and cell culture and regenerative medicine[10].

A number of papers introduced cellulose acetate can be electrospun using several solvents: acetone, acetic acid et.al[7]. For the scaffold application, it also been used for producing stable and functional active cell networks[8,9].

In Han's paper, he used CA as raw material to fabricate the three-dimensional extracellular matrix. Acetone was the solvent to dissolve CA. Since electrospinning technique can produce fibers with nano or micrometer diameter, the electrospun fibers are similar with the 3-D extracellular matrix. Three different concentrations were prepared and three pairs electrospinning parameters were used to make 3 layers CA electrospun fibers. That's a succeccful attempt of CA's biomedical applications[9]. Another one is like making CA template for promoting cardiac cell growth. After preparing the CA template, the cardiac fibroblasts proliferation time has been recorded. It concluded CA is a better cardiac fibroblast template than many other materials, like PS, GL and PCMS. At last the lost weight for CA has been tested after 24 days at 37 centigrade, PH 7.2[8]. It proved CA is a biodegradable material.

The advantages of CA fiber is that it is soft, smooth, dries quickly. But it also has some disadvantages: weak strength fiber and quickly loses strength when being wet and poor thermal retention. Since many excellent properties and the poor characteristic - low strength of CA fibers, what people need to do is add strength to it.

1.3 PVP-CA Composite and Synthesis Mechanism

1.3.1 Composite Materials and Methods of Preparing PVP-CA composites

Composite materials are made from at least two constituent materials and have significantly different properties. When these individual materials are combined, a new material will be produced -- the composite materials (briefly as composites), which has remarkably different properties than the individual materials used to produce it, this makes composites really different from the conventional materials.

What's more, composites have many other advantages like strong, lighter, cheaper, enhanced mechanical properties and design flexibility. Another kind of composites, the nano-composites, are similar to the traditional composite, but they can provide some other good properties than the composites. For instance, they have large surface area, ultrafine structure, high surface reactivity and strong interfacial bonding[11,12]. However, both the composites and the nano-composites have a same disadvantage: right now, no optimized techniques have been found for material processing. Different fabrication technology will produce totally different materials. The scientists are focus on finding better ways to synthetize composites.

Methods to prepare PVP and CA composites

Cellulose acetate can be produced as membrane that has many applications. People tried to use casting technique to treat CA and its suitable solvent to make membrane[13] Since many parameters may affect the fabrication of membranes, like polymer concentrations[14], the casting film thickness[15], the presence of additives[16], coagulation bath temperature[17] and the presence of some other solvents[18]. In these parameters, additives and coagulation bath temperature are the 2 significant ones. Scientists tried to add PVP, concentration (at 0, 3, 6wt%)as additives under different coagulation bath temperature(at 0, 25, 50 °C) to make CA membranes. The result was when concentration of PVP increased from 0wt% to 3wt%, the membrane had more macrovoids. But the number of macrovoids in membrane decreased when concentration of PVP increased from 3wt% to 6wt%[11] This is because the presence of PVP has dual effects to the CA membranes. On one hand, from 0 to 3wt% of PVP, since it is a hydrophilic material has non-solvent abilities, when it has been added into the membrane fabrication system, it has relatively low affinity to the solvent NMP and the CA material. Then the PVP increased the thermodynamic instability, that's why much more macrovoids had been formed in the membrane structure. However, from 3wt% to 6wt%, with the increasing of PVP, the viscosity of the solution increased. The higher viscosity of the system may decrease the flow rate and the diffusion exchange rate during the membrane formation. This formed a denser structure of the membrane, thus the number of macrovoids in membrane decreased. In one word, different amount of PVP has totally different effects when it treated as additives.

Using electrospinning technique, fibrous membranes of cellulose acetate and PVP has been formed from two different length needles[19]. The researchers used CA and PVP dissolved in many different solutions, like ethanol, water, acetone and acetic acid. Also, different flow rate and different collector distance have been used. By changing these parameters, different diameter

electrospun fibers had been formed. The main difference from conventional electrospinning is the various length of two needles. PVP and CA solution were pumped into two different syringes and of course two different needles were used. Because the length of needles were not same, the distance between each needle tip and the collector was obviously different. Then two kinds of CA-PVP composites were made. When PVP was pumped into the longer needle, CA was in the shorter needle, electrospun fibers were PVP in the center and CA at the surface- the CA/PVP/CA composite. On the other way, PVP/CA/PVP fibers were made with CA in the longer needle, PVP in the shorter one. After successfully prepared the PVP-CA electrospun fibers, the mechanical test was proceed to the samples. The result showed PVP/CA/PVP fiber had higher value of strain at break and lower value of tensile strength compared with CA/PVP/CA fiber due to the high strength property of PVP and excellent tensile capacity of CA.

Some people also compared the PVP and CA when prepared for biomedical scaffold application. Because hydroxylapatite is a main composition of natural bone, good capability to combine with it should be a main consideration for preparing tissue scaffolds[6]. Electrospinning technique was used. Different concentrations of PVP or CA with hydroxylapatite in different amount of solvent were prepared. After electrospinning, all the fibers were heat treated and calcination. From the SEM images and XRD spectra, samples of CA with acetone and acetic acid fibers showed excellent and homogeneous HA dispersion than PVP electrospun fibers in the polymer matrix. The reason might be the interaction between the HA and both the acetone and acetic acid.

Another paper discussed composites electrosun fibers using two syringe and two different needles. While, coaxial electrospinning using coaxial needles are able to produce PVP and CA

core-shell fibers. Same recipe of PVP and CA was used as[19]. Both CA-PVP core-shell nanofiber and PVP-CA core-shell nanofiber had been produced. After washing, PVP in the samples was removed since PVP was water soluble. The TEM and SEM showed the core-shell structure and the fiber morphology after experiment. FTIR proved the existence of both PVP and CA and the disappearance of PVP after washing. After that, the fibers were used as drug delivery template. The drug and electrospun fibers were immersed into 400ml buffer solution. After certain time, 1ml of buffer solution was taken out and did the UV-vis spectroscopy test, the absorbance wouldn't be same with different amount of drug. When the absorbance was stable, the time used for drug release was the drug release time. Different release time of amoxicillin in PH 3.0 or 7.2 was tested. The release time of amoxicillin at PH is 3 was 3 times longer than PH is 7.2[3]. The researcher concluded it might because the existence of hydrogen-bond between amoxicillin and both PVP or CA in a acid environment.

What's more, PVP has been used as additives to form CA membranes for ultrafiltation of metal ion[20]. Similar as reference[11], PVP was used as additives in CA membrane formation because its excellent miscible with CA. Different weight of PVP: 1, 2, and 3wt% was added into CA and DMF solution. The technique used for preparing CA-PVP membrane was the stirring and casting method. FTIR, Thermogravimetric analysis and SEM was proceed to know the exact characteristic of CA-PVP membranes. In FTIR spectra, different peaks show the existence of PVP and the intermolecular interaction between the PVP and CA. The TGA spectra told us PVP was really added into the CA membrane due to the different weight lose at same temperature for various PVP weight. Since the main purpose was preparing membrane with much more numbers of pore, testing about the percentage of pores in the membrane showed with the increasing of PVP weight, number of pores was increased too. However, for the pore radius, PVP helped

making small pore and improved the pore density. These two parameters were very significant for ultrafiltation membranes. Then the membranes were used for pure water flux test and heavy metal separation studies. Both the two experiment shows adding PVP improved the water and metal solution flux ability, shorten the flux time.

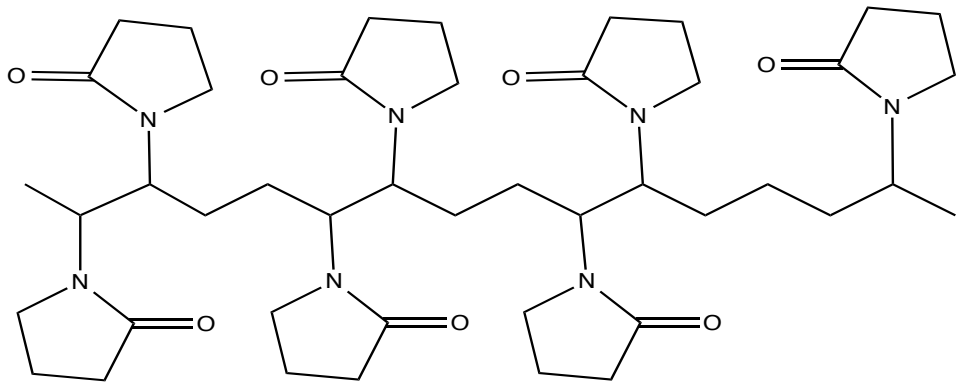
All of these works have been done by other researchers. They used various ways to prepare PVP-CA composites, like the solution casting and the electrospinning. The applications for the PVP-CA composites are also in many aspects, for instance, drug release template, tissue engineering scaffold or the ultrafiltration membranes. Thesis works means PVP-CA composites really have excellent properties than each of them. Further researches about PVP-CA fabrication method and applications are undergoing.

1.3.2 Synthesis Mechanism of PVP and CA Composites

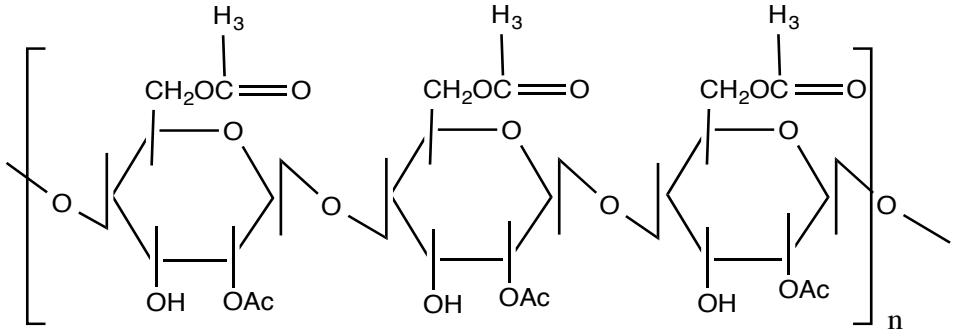
PVP and CA, which are both low toxic and biodegradable materials. PVP has its own C-N and C=O chemical groups and Cellulose acetate has O-H or $COOCH_3$ functional groups. So the water soluble PVP can permeate into the network of cellulose acetate. PVP has excellent miscible capability with CA membranes. Then the abundant C-H or O-H groups in cellulose acetate will have a strong connection(hydrogen bond) with C=O group in PVP[3]. Because of this, a aligned uniform PVP-Cellulose acetate composite can be obtained.

The reason why PVP and CA composites are useful is the presence of both C-N and C=O in PVP could provide more electron bond[21] which made it's easier to adsorb some ions, then have better ability to combine with other chemicals.

For example, when PVP-CA composites fibers are contact with Ca^{2+}, the Ca ions will quickly attach itself to two adjacent carbonyl groups. The two C=O groups can donate two pairs of lone pair electrons, there will be an chemical attraction between these two pairs of lone pair electrons. What's more, since both acetic acid and acetone has C=O group, so PVP and CA composites in the acetic acid and acetone solution will have sufficient C=O group to react with other chemicals.



PVP



Cellulose Acetate

The inspiration of preparing PVP-CA composite is CA has good extensibility but weak mechanical strength. However, PVP is commonly treated as strength polymer. That's why PVP can add strength to CA materials. What's more, both PVP and CA are relatively cheap polymer with excellent biocompatible and biodegradable properties. All of these reasons made preparing PVP-CA composite is a good way for further applications.

Figure 3 is the mechanism between PVP and CA

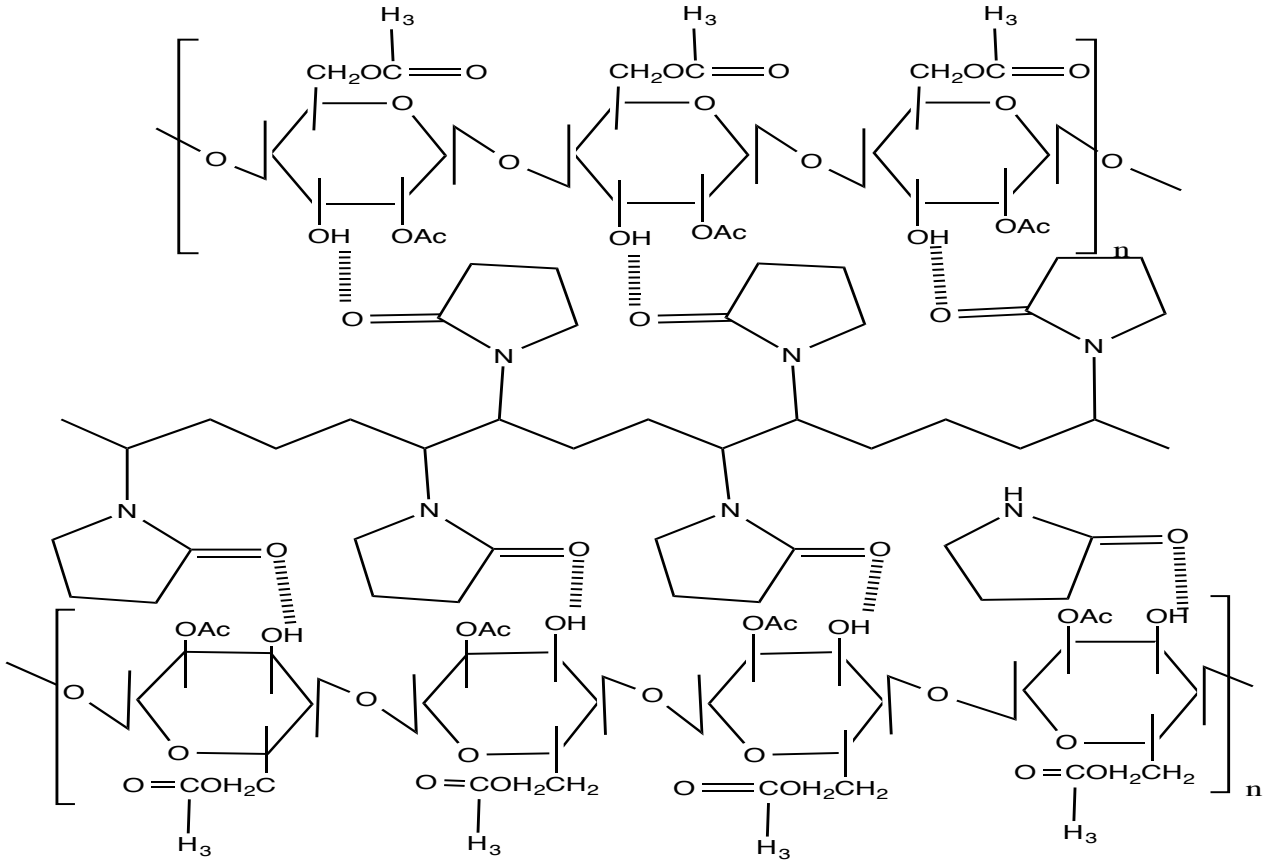


Figure 3*: Possible mechanism of PVP and CA composites*

1.4 Electrospinning technique

In recent years, electrospinning has emerged into scientists' eyes as a powerful technique for the fabrication of nano or micro-fibrous materials. Electrospinning technique has become popularity in the last 10 years due to the increased interest in nanoscale properties and technologies. This technique allows for the production of polymer or ceramic fibers with diameters varying from several nanometers to greater than 1 micrometers.

Electrospun fibers have many excellent properties that made them as attractive materials for a range of applications: including high specific surface areas, high porosities (up to 80%), and controllable diameters (from nanometers to micrometers). The fiber can be composed through the blending, emulsion reaction, encapsulation, and immobilization of biological and other active components. Therefore, electrospun nanofibers show great promise in biomedicine, tissue engineering, water and air purification.

Electrospinning uses the electrical charge to draw very fine fibers from many kinds of liquid(emulsion or solution).When the high enough voltage applied to the liquid droplet, the liquid becomes charged. So the electrical repulsion will counteract the surface energy, then the taylor cone will appear[26]. The droplets can be stretched and the liquid will be dried during the flight. Figure 4 is the schematic electrospinning set-up. Due to the production procedure, the electric field, distance from the needle to the target, flow rate, the concentration of the solution and some other parameters are the significant influence factor that can decide whether the electrospinning is successful or not and the diameter of the fiber.

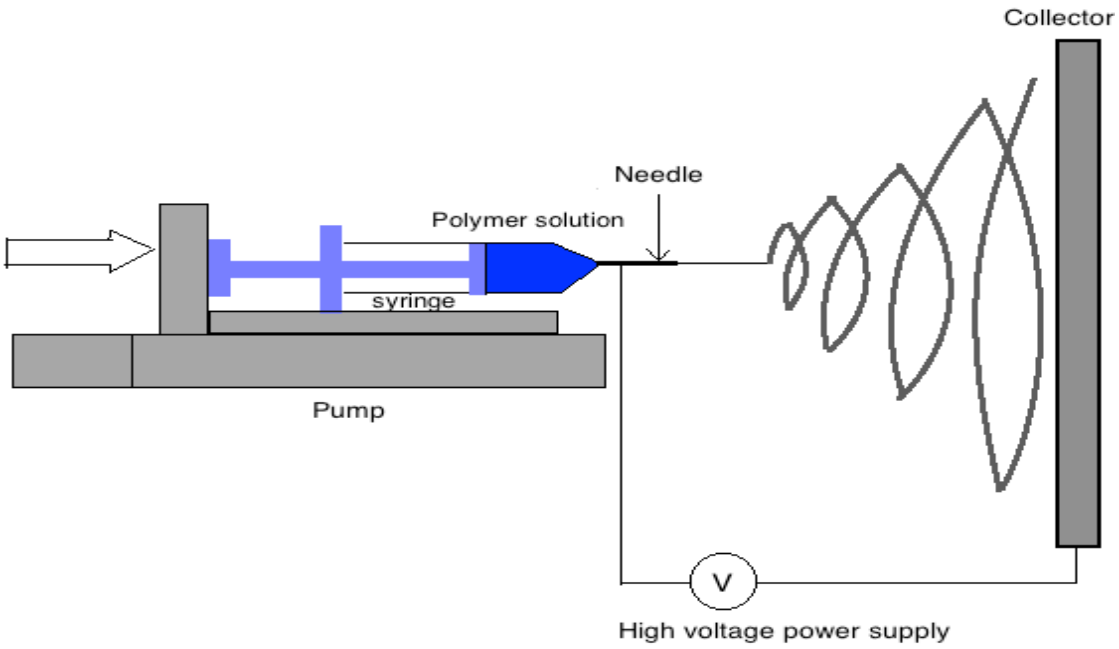


Figure 4*: Schematic electrospinning set-up*

1.4.1 Parameters that effect electrospinning and the application

Concentration

Every solution has its own limit of concentration to process the electrospinning, mostly between 5%w/v to 35%w/v. With relatively high concentration, larger diameter fibers will produced[22]. What's more, low concentration will induce the form of beads in the fibers. With the concentration of the solution increased, the much smoother and uniform electrospun fiber can be produced[23].

Flow rate

During the elctrospinning, the pump can provide accurate flow rate to the solution. However, every pump has its own parameters. With different syringe diameter, the flow rate should be

different. Table 1 is the size of different syringes and the relevant flow rate for them.

Table 1: Syringe Pump Flow Rates by KD Scientific

Syringe	Diameter	Minimum flowrate rate	Maximum flow rate
10ul	0.46 mm	0.001 ul/min	0.350 ul/min
25ul	0.73 mm	0.001 ul/min	0.884 ul/min
50ul	1.03 mm	0.001 ul/min	1.759 ul/min
100ul	1.46 mm	0.001 ul/min	3.526 ul/min
250ul	2.3 mm	0.01 ul/min	8.78 ul/min
500ul	3.26 mm	0.01 ul/min	17.65 ul/min
1ml	4.61 mm	0.1 ul/min	35.2 ul/min
2.5ml	7.28 mm	0.1 ul/min	88.0 ul/min
3 ml	8.59 mm	0.1 ul/min	122.5 ul/min
5 ml	10.3 mm	0.1 ul/min	176.2 ul/min
10 ml	14.57 mm	0.001 ml/min	0.351 ml/min
20 ml	19.05 mm	0.001 ml/min	0.602 ml/min
30 ml	21.59 mm	0.001 ml/min	0.773 ml/min
50 ml	28.9 mm	0.001 ml/min	1.387 ml/min
60 ml	26.6 mm	0.001 ml/min	1.175 ml/min

Similar to the effect of concentration, lower flow rate will get small diameter fibers[24]. Higher flow rate may not have enough time to dry the fibers[25], the experiment will fail

because of this. What's more, high flow rate will not form taylor cone at the end of the needle, so uniform fibers cannot be produced.

Voltage

Researchers always use proper voltage to create an electric field to overcome the liquid surface tension. With the increase of the voltage, the liquid at the end of the tip will be elongated and a conical cone- taylor cone will formed[26]. When the voltage is high enough, the charged jet can eject from the tip of the needle and dried then collected on the metal collector. Always, the voltage will use KV as unit and lower than 30KV. If the voltage is too high, it may create beads in the fibers[27].

Distance from the tip to the collector

The distance is another important factor of the elctrospinning. It should be long enough to dry the fiber, or liquid solution will be collected and the diameter cannot reach nano or micro grade. When the distance is long enough, fiber diameter decreased with increasing distance[28].

However, beads will formed either distance is too close or too far away[29].

Needle design

Size:

Obviously, different needle can produce different fibers. Large needle size will attribute to larger diameter of fibers than small needle gauge because of different diameters of needles. Table 2 is the size of different needle gauge.

Table 2: needle gauge size

Gauge	Inner Diameter(mm)	Outer Diameter(mm)
14	1.75-1.79	2.08-2.14
15	1.49-1.53	1.81-1.85
16	1.33-1.37	1.63-1.67
17	1.15-1.19	1.46-1.49
18	0.97-1.01	1.25-1.29
19	0.77-0.81	1.04-1.08
20	0.62-0.66	0.90-0.92
21	0.54-0.58	0.81-0.83
22	0.44-0.48	0.71-0.73
23	0.39-0.43	0.63-0.65
24	0.31-0.36	0.55-0.58
25	0.28-0.32	0.50-0.52
26	0.24-0.28	0.45-0.47
27	0.22-0.24	0.40-0.42

Some other methods showed different needles when electrospinning materials:

Multiple jets electrospinning[30]:

By design new equipment with multiple jets, the output of electrospinning can be highly improved. A researcher designed a matallic source disk with holes in it, like figure 5. This disk

was treated as the traditional needles. Since this disk has 24 hole inside it, the output of the electrospinning technique can improved significantly. From the scentific calculate, the holes on disk was designed with a 45 degree angle to the plane of the disk. Then a tube was placed between the syringe and the center of the disk. The fluid solutions were pumped into the syringe and through the tube into the disk. After that, ejecting from the 1mm diameter holes at the edge of the disk[30]. High electric field were absolutely existed between the disk and the cylinder-shaped collector. From this technique, the flow rate was as high as 0.3ml/min to 0.4ml/min, which was 10 to 12 times higher than the traditional single needle electrospinning technique.

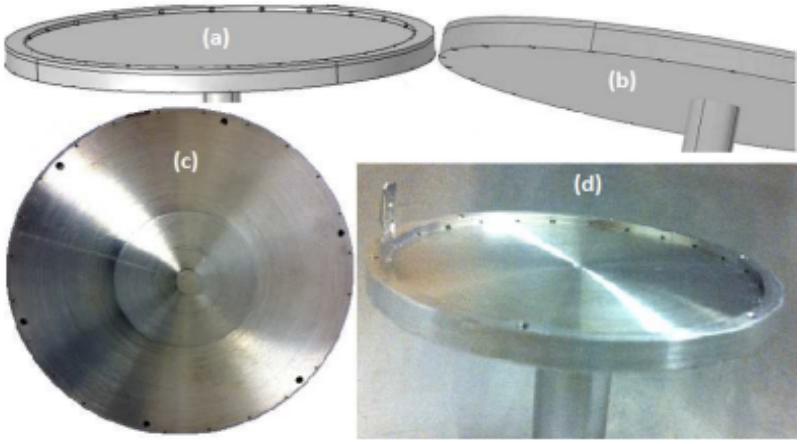


Figure 5: Side, bottom and top view of the electrospinning disk ***(S. sood, G. Zheng and P. Gouma. High throughput synthesis of ceramic nanofibers. 2013 MRS Meeting)***

Coaxial needles

Coaxial electrospinning is an extension of conventional electrospinning, From coaxial electrospinning we can get ultrafine fibers than single needle set up. The structure of this kind ultrafine fiber is the core-shell fiber. This special fiber can only achieved from the special set-up. So the coaxial electrospinning comes with a dual-capillary spinneret, where a capillary is

surrounded by a larger one. Thus, two syringes are necessary and also two pumps are needed, then the high voltage and the collector. Like the set-up in figure 6[31]:

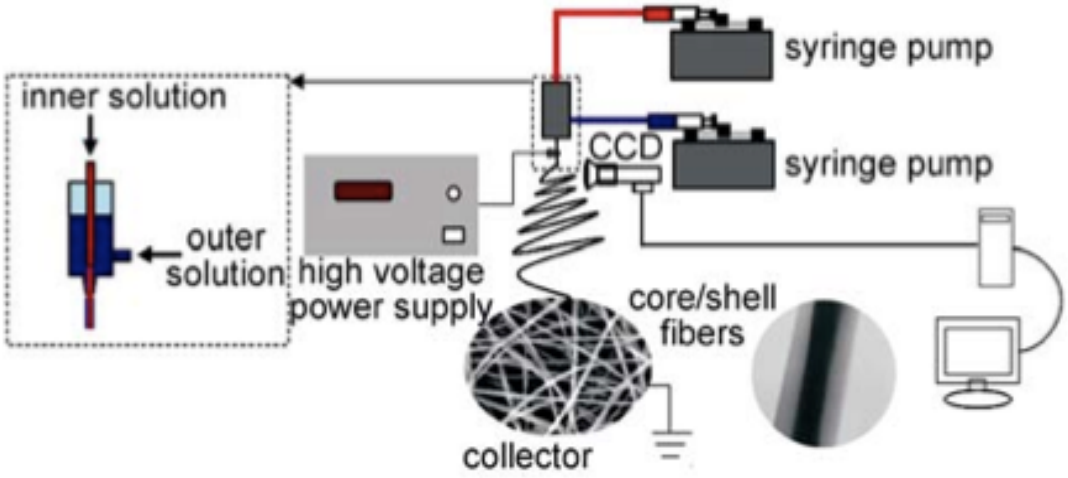


Figure 6*: Schematic setup of coaxial electrospinning (H.Zhang, C. Zhao, Y. Zhao, G.Tang and X. Yuan. Electrospinning of ultrafine core/shell fiber for biomedical application. March, 2010)*

Since two syringes are needed, two solutions are also needed. Generally, polymer solutions are suitable for the coaxial electrospinning. A polymer solution is treated as the outer one to form the shell, then another polymer solution or the small molecule solvent can be put in the inner spinneret as the core.

Due to the inner needle is surrounded by the outer one, the two materials will meet each other at the edge of the spinneret. As same as the conventional electrospinning, a Taylor cone forms from the tip. When the voltage is high enough to overcome its surface tension, the core/shell jet will eventually formed on the collector [32-36].

For the outer solution, If the core fibers are important to the application, when the core/shell

nanofibers formed, the shell can provide protection to the core fibers. Otherwise, if we need to use shell fibers, some hard materials should be considered as the inner solutions or the additive to the inner solutions. Then the core fibers can add strength to the core/shell nanofibers, improving the mechanical property of the electrospun fibers.

From the application point, core-shell fibers have many excellent usages: *Yu et*[37]paper the writers used the modified coaxial electrospinning process prepared polymer fibers from a high concentration solution. What's more, for ketoprofen loaded cellulose acetate nanofibers and gelatin added polyvinyl alcohol nanofibers, the mechanical property of them has been improved[38,39].

Polymer molecular weight

To reduce the numbers of the beads in the fibers, we should increase the molecular weight of the polymer[40]. What's more, the droplets are formed if the molecular weight is not high enough.

Designation of the collectors

First of all, the collector should be metal or covered with conductive material, like the aluminum foil. Then electric field will exist between the needle jet and the collector. If smooth fibers are required, the ground metal collector should be considered. However, if people need porous fibers, then they should choose porous collectors[41,42].

Right now, most commonly collectors are flat ones. The nanofibers obtained from flat collectors are non-wowen, which cannot be used in many applications. On the other hand, the uni-aligned nanofibers have better mechanical property and unlimited applications. But it is not

easy to obtain the uni-aligned nanofiers. From the collector designation point, scientists found 3 methods to achieve the aligned nanofibers[43].

A cylinder collector with high rotating speed

Some scientists tried rotating collector to achieve aligned fibers[44,45] However, the rotating speed should be higher than the fiber alignment speed, which is the fiber evaporate speed. If the collector rotating speed is lower than alignment speed, non-woven fiber will still be formed. However, the over fast rotating speed will break the fiber. So a limit rotating speed is important to get the successful continuously fibers. That's why the correct rotating speed is not easily to obtain.

A sharp edge thin wheel collector

Like a cylinder collector, the wheel collector also has a linear speed. In[46], the researchers used 22m/s as the speed for the wheel collector. Since the wheel collector has a sharp edge, this tip will be the nearest part of the collector to attract the fiber. That's why the rotated sharp edge thin wheel collector can successfully obtain aligned fibers. What's more, the distance between two fibers might be large because every fiber was charged, they were repulsed by each other. From this point, new method to collect much denser fibers should be considered.

A frame collector

Frame collector means put a frame, which is best to be the metal collector, between the charged needle and the ground collector. The frame should have a inclination angle to the ground collector then the fiber can be collected between two edges of the frame. Some more works about what the inclination angle should be and rotating the frame to produce much more aligned

fiber are undergoing[43].

Other parameters

Temperature, humidity[47-49] and wind will affect the formation of the fibers. Increase temperature will decrease the viscosity of the solution then smaller diameter fibers can be achieved. The humidity may cause some pores in the fiber and the wind in the fume hood also will stretch the fiber then bring effect to the structure of the fiber.

Applications of electrospinning

In the biomedical application fields, electrospun nanofibers can be used in many aspects, such as the drug delivery, tissue engineering scaffolds and wound healing or implants in surgery[50]. Also, electrospun fibers have some Potential applications, such as filtration membranes, catalytic nanofibers, enzymes, fiber based sensors[48] and some energy storages(solar cells and batteries)[51]

The application of electrospun fibers in biomedical field, like tissue engineering scaffold and drug release area have been discussed before. But for the sensor, catalyst and energy storage applications, some works has already done.

Catalyst: For the electrospinning technique, when the molecular catalyst embedded into the nanofibers, it might leak out the matrix because the specific structure of the nanofibers. It should be better when catalysts were coating onto the surface of the fibers. This thin layer can show a pretty good catalyst retain ability. TiO_2 always be used as catalyst.

Sensor: Materials that can be used in sensor should have high sensitivity, selectivity and fast

response ability[52]. Always the sensors are in small dimension and are relatively cheap materials. Some electrospun polymers have been treated as sensors, like the PAA, PMMA and PAN. In some papers, the polymer electrospun fibers have successfully detected the existence of certain materials. Electrospun fiber sometimes showed better sensing capability that might because the specific nano-structure, which is better than traditional casting and spin coating technique. The sensor materials can possess a higher specific surface area.

Energy storage: Right now, the solar cells, fuel cells and lithium ion batteries are the main sources to storage energy. Since specific electrospun fibers have high specific surface area and really perfect electrical conductivity, it is suitable for using in the solar cells. What's more, the electrospun fibers specific structure and nano-sized diameters made it becomes an important component in fuel cells (catylists) and lithium ion batteries (seperators).

CHAPTER 2 EXPERIMENTAL DETAIL

2.1 Materials processing

Preparation of PVP and CA composites

PVP: Typical Mw: 1,300,000(LS)

CA: average Mn: 50,000 by GPC

Acetic Acid: Glacial by ACS reagent grade

Acetone: General use HPLC-UV Grade Reagent Grade ACS/USP

First, the 7.5%, 10% and 17.5%w/v composites have been produced using acetic acid and acetone as solvents. The recipes are below:

Table 3: Recipe of 7.5%,10% and 17.5%w/v PVP-CA composite

Concentration	PVP	CA	Total weight	Acetic acid	Acetone	Total volume
7.5%	0.25g	0.5g	0.75	6ml	4ml	10ml
10%	0.333g	0.667g	1.0	6ml	4ml	10ml
17.5%	0.583g	1.167g	1.7	6ml	4ml	10ml

Then, the solution was ultrasonicated for 1 hour or more until a transparent homogeneous solution was achieved. Then the solution was left for one night for further reaction between polymers and the solvents.

The next day, solution was transferred into a 10ml syringe. And a 20 gauge needle was used for electrospinning. Then the syringe was fixed onto a pump: Kd Scientific flowmeter. The collector is a glass plate that has been covered with aluminum foil. Teflon was sprayed onto it to

help get smoother fiber and the fiber will be much easier to tear up after electrospinning. The distance between the needle tip and the collector is 15cm for all three solutions. Then the flow rate for 7.5% and 10%w/v is 0.03ml/min, but for the 17.5% w/v solution, the flow rate is 0.08ml/min. Since all the solutions use 10ml solvent, the electrospinning process lasted for more than 5 hours for 7.5% and 10%w/v solutions and about 2 hours for 17.5%w/v solution. Figure 7 is the electrospinning set up in our lab.

Figure 7*: electrospinning set-up*

In order to supply an electric field, a Gamma High Voltage Research DC Voltmeter was used. Since the voltage range of this voltmeter is up to 30kv, the voltage for 7.5% and 10%w/v is19kv and for 17.5%w/v is 16kv. One of the two electrodes was connected to the needle and the other one was connected to the collector. Then the electric field was established. The setup was put into a fume hood to avoid harmful scent came out.

Since the polymer is sticky, the set up needed to be checked all the time during the electrospinning to avoid clogged needle. Then after the electorspinning, the needle should be cleaned and put back into the ethanol or acetone solvent to dissolve the polymer in the needle.

Once the electrospinning has finished, the fiber was peeled off from the collector and kept into vials.

Figure 8 is the PVP and CA composite fibers after electrospinning

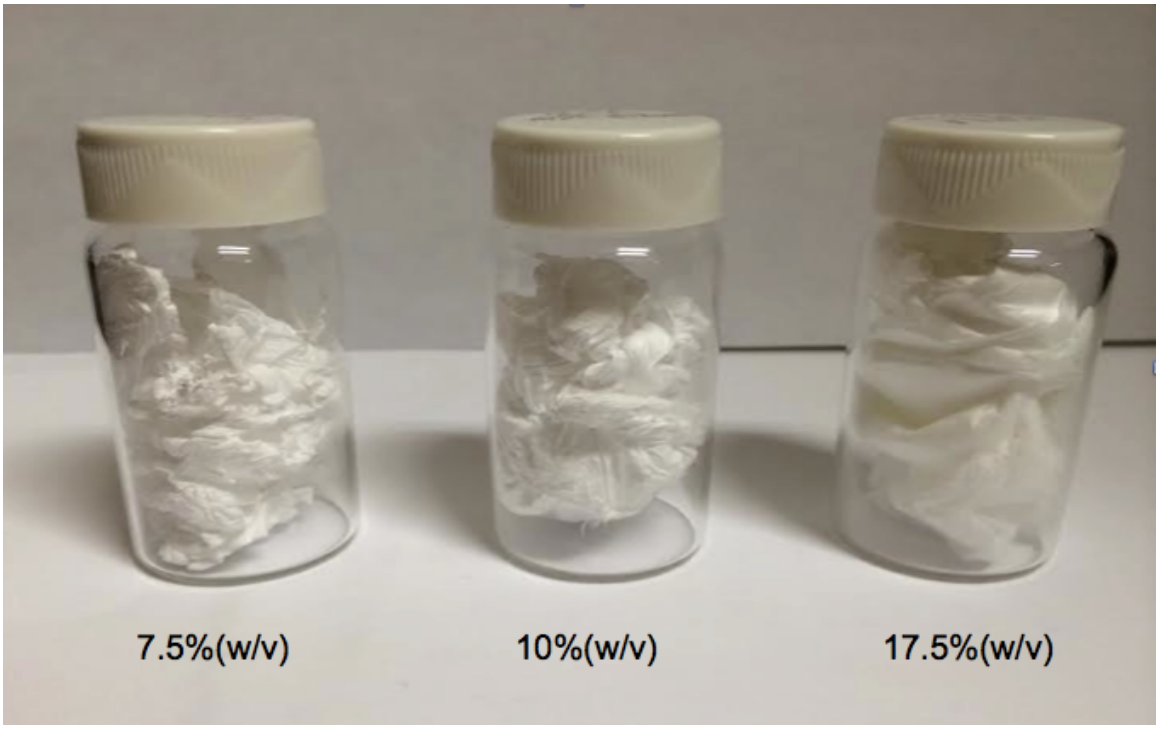


Figure 8*: 7.5%, 10% and 17.5% electrospun fibers*

Preparation of two-layer PVP and CA electrospun fibers

The solution of first layer is the PVP in water, and second layer is CA in acetone. Same PVP and CA used as the raw material as the preparation of the composites.

The recipes are below:

PVP layer: 0.1mM PVP in water (1.3g PVP in 10ml water)

CA layer: 10% CA in Acetone (1.0g CA in 10 ml acetone)

Same electrospinning set-up was used as producing PVP/CA composites. The flow rate for PVP in water was 0.03ml/min, the voltage between needle and collector was 19KV. For CA in acetone solution, flow rate was 0.045ml/min and voltage was 22KV. For both polymers, the

distance between needle tips and the collectors were15cm. For further characteristic test, the fibers for both composite and two-layer fiber were cut into 3cm*3cm pieces.

Figure 9 is the two faces of the two-layer PVP and CA fibers. PVP face is smoother than CA face.

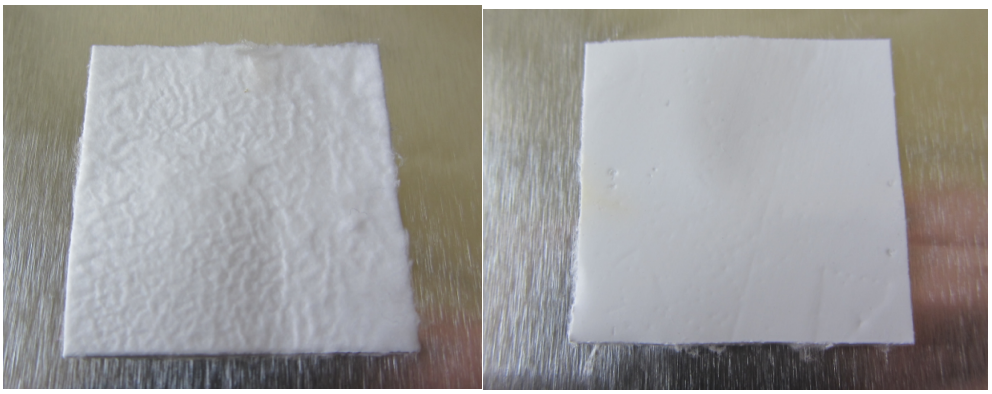


Figure 9*: left image is CA surface and right one in PVP surface*

Preparation of each layer electrospun fibers and their comparable fibers

Compared with the two-layer electrospun fibers, each layer was produced and collected. CA in acetone and PVP in water solutions had been prepared.

The recipe of materials and Electrospinning parameters are below:

Table 4: Recipe of electrospinning

Material	Concentration	Flow rate	Voltage	Distance
CA in acetone	10%w/v	0.045ml/min	22kv	15cm
PVP in water	0.1mMw/v	0.03ml/min	19kv	15cm
PVP in water	25%w/v	0.045ml/min	22kv	15cm

2.2 Characterization Techniques

SEM

Scanning electron microscopy(SEM) is a electron microscope. It can provide images of a sample by using focused beam of electrons to scan it. SEM helps to observe and characterize the surface structure of many kinds of materials from nm to um grade. When doing 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 topography and composition can be received. The samples need to be put into the vacuum atmosphere. SEM is popularity because it can provide 3-D structure images for the samples.

Since polymers are not electric conductive material, before SEM test, some preparation should be done, like coated with an ultrathin electrically conducting material, for instance, gold, tungsten or chromium. Then the sample should be cut in an appropriate size since the specimen chamber is not big enough. Besides, the sample need be fixed onto the conductive tape for successful testing.

Raman spectroscopy

Raman spectroscopy is a technique that used to observe the existence of some specific chemical groups from the rotation, vibration and other low-frequency modes in a system. The laser light can interact with the motion of the groups, resulting in energy shifting. This energy shifting shows information about different vibrational or rotational modes in the system. When the laser light interact with the electron cloud and the particular bonds, the light scattering will excite the molecule from the ground state to a higher energy state.

2.3 Hydrophilic, Oleophilic and Oil Absorption Test

Hydrophilic and Oleophilic Test

Before process the oil absorption test, hydrophilic test should be proceed at first. 3cm*3cm pieces of 10%%w/v, 17.5%w/v composite and 2-layer PVP-CA fibers were prepared. Then 2 drops of water dropped onto each fiber.

Same test was proceed for Oleophilic test using No.6 oil.

Oil Absorption and its Comparison Tests

No.6 oil was used to proceed the oil absorption test. Two group tests were employed. The first group was the 10%w/v and 17.5%w/v composite. The other one composed of the 17.5%w/v composite and two-layer PVP-CA fibers. Samples weight had been recorded before and after absorption.

CHAPTER 3: RESULTS AND DISCUSSIONS

3.1 Materials Characterization

To study and analyze the surface structure and the difference of fiber diameters, the SEM images were taken of all concentration PVP-CA composite fibers and the each single layer of the two-layer electrospun fibers.

Figure 10-12 are SEM images of PVP-CA composite

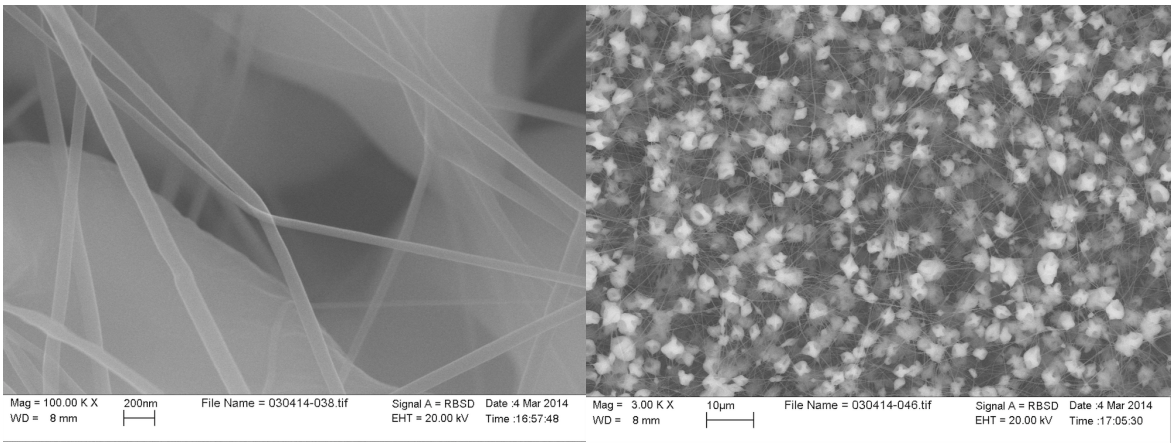


Figure 10*: SEM of 7.5%w/v PVP and CA composite*

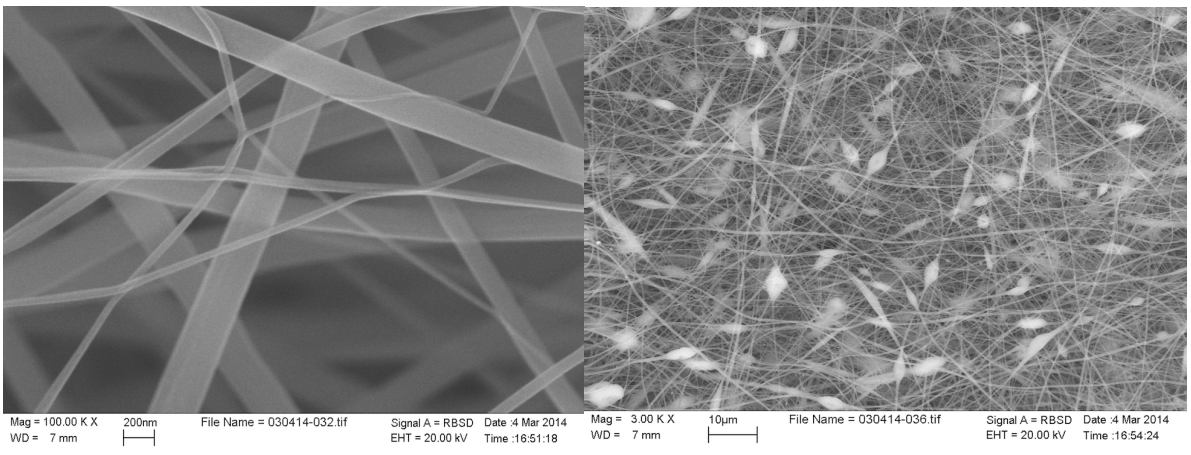


Figure 11*: SEM of 10% PVP and CA composite*

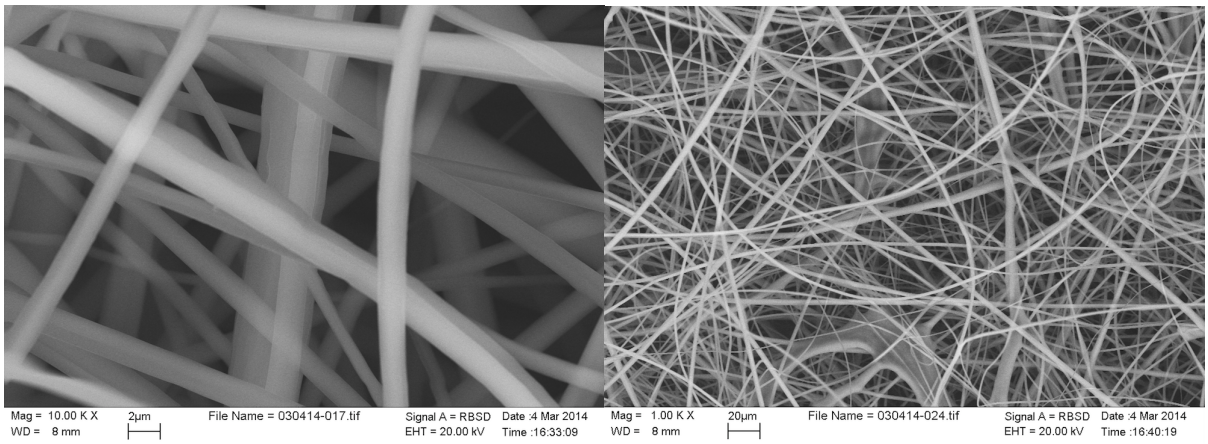


Figure 12*: SEM of 17.5%w/v PVP and CA composite*

From SEM images, the diameter of electrospun fibers increased from 7.5% w/v to 17.5%w/v. The fibers' average diameter of 7.5%w/v is less than 100nm. For 10%w/v electrospun fibers, the average diameter is 200nm or less. However, the diameter of 17.5%w/v fibers is between 1um and 2um. It is because the effect of three parameters: concentration of solution, electrospinning voltage and flow rate value. Increasing concentration of solution, decreasing voltage and increasing flow rate will induce the higher diameter electrospun fibers.

What's more, 7.5%w/v nanofiber has a lot of beads in it. The amount of beads decreased when concentration becomes higher. When concentration of fibers is 17.5%w/v, there's almost no bead in the fiber. This fits the conclusion of many other people's work. Moreover, the voltage for preparing 7.5%w/v composite was 19kv, which is 16kv for both 10%w/v and 17.5%w/v composite. Higher voltage may lead to the formation of beads.

Figure 13 is SEM of CA in Acetone

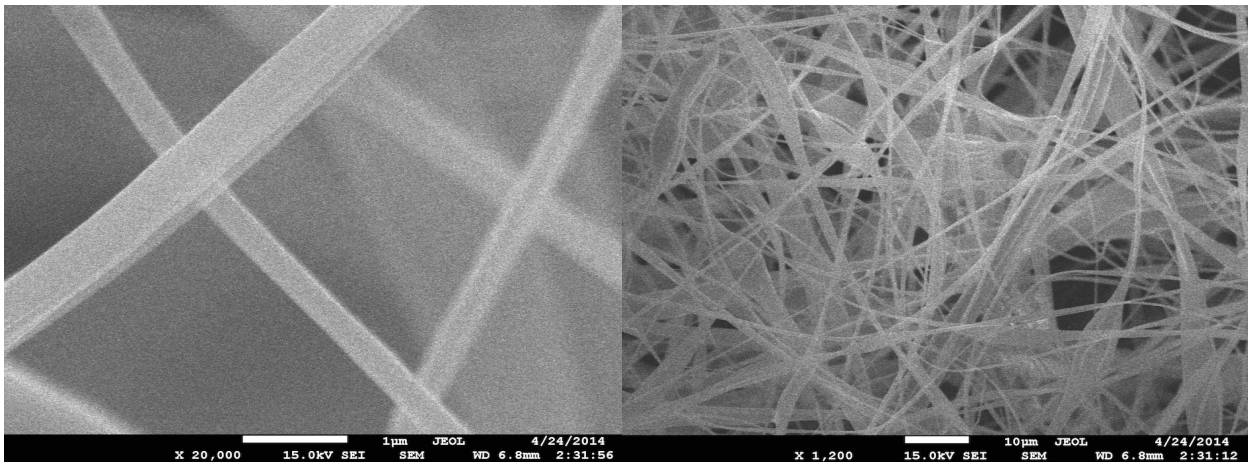


Figure 13*: SEM of 10%w/v CA in acetone*

Figure 13 shows the diameter and distribution of CA in acetone electrospun fibers. The average diameter of 10%w/v CA in acetone fibers is 300 to 500nm. The diameters of CA fibers are not very aligned. However, better than 7.5% or 10%w/v CA-PVP composites, CA in acetone fibers do not show much beads.

Figure 14 and figure 15 are SEM images of 0.1mM PVP in water and 25%w/v PVP in water fibers

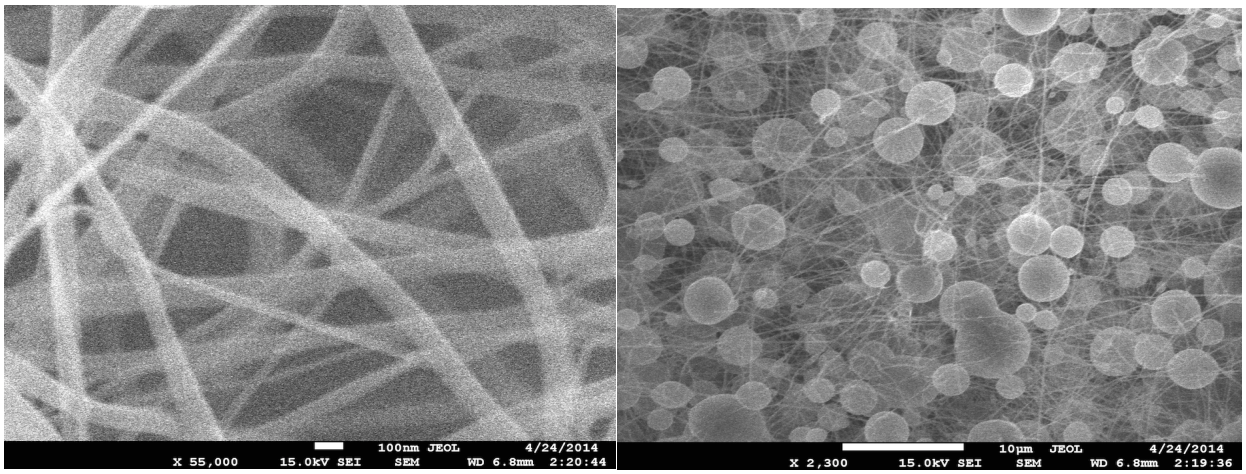


Figure 14*: SEM of 0.1mM PVP in water*

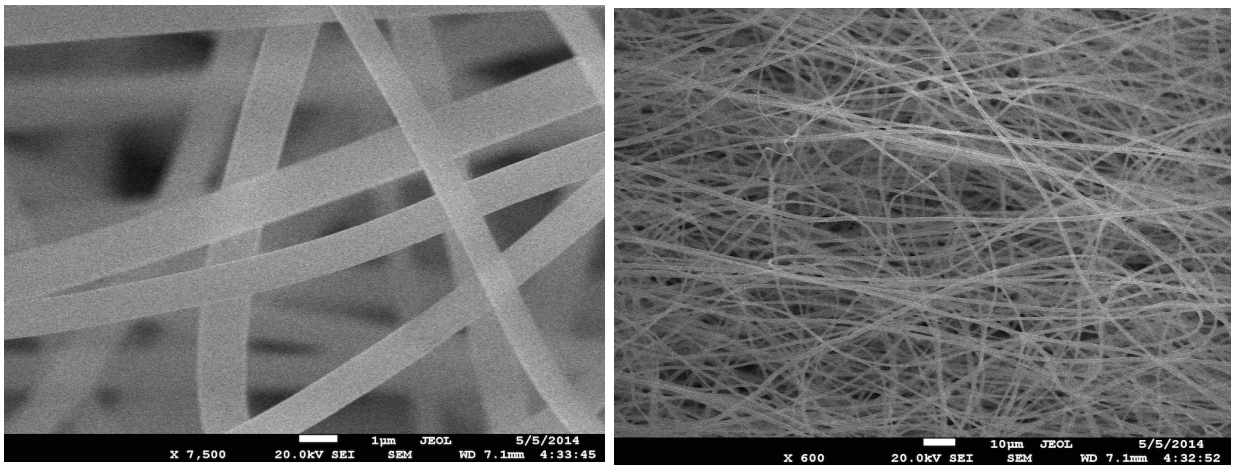


Figure 15*: SEM of 25%w/v PVP in water*

In figure 14, some beads exist in 0.1mM PVP in water, but in figure 15, 25% PVP in water fibers are bead free. This also concludes that increasing concentration of solution can decrease the beads. For the fiber diameters in both concentrations, increasing concentration really resulted in the formation of larger fiber diameters.

Figure 16 is SEM of 25%w/v PVP in water (After 1 year exposure to air)

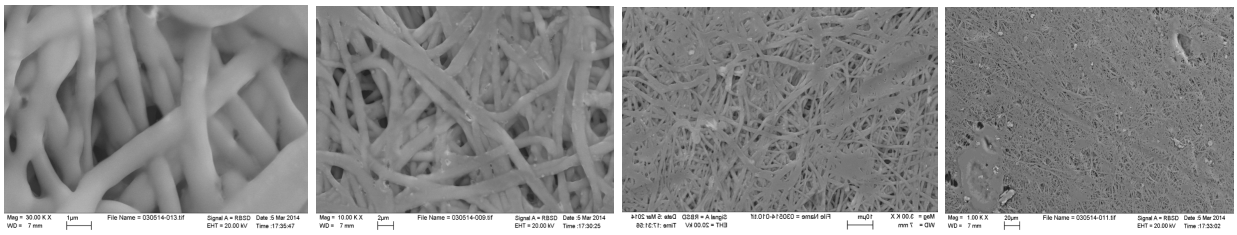


Figure 16*: SEM of 25%w/v after 1 year exposure to air*

Figure 16 is a comparison sample of 25% PVP in water electrospun fibers. Compared figure 16 with figure 15, since these two samples have same recipe, the fibers in these two images have similar diameter, around 1 um. The range of fiber diameter is really narrow which means the fibers have almost same diameter. This is a big advantage of PVP fibers compared with CA in acetone fibers. Figure 16 shows SEM images of PVP fibers with scale from 1um to 20um. We can see that since this sample has been kept in the air for a long time, the PVP fibers

are sticking together after absorbing water in the air and turned to be transparent. It almost turned to a whole membrane without fiber inside. Like figure 17:

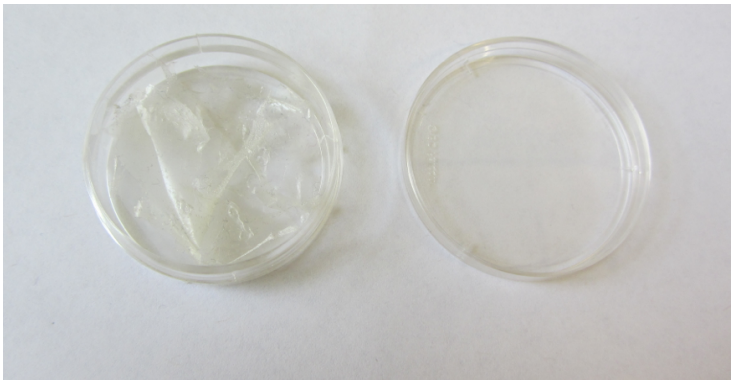


Figure 17*: 25% PVP in water (after a year exposure to air)*

Analyzing of the Raman results

To characterize the different structure between PVP-CA composite and CA in acetone fibers, the Raman spectroscopy testing was conducted. Figure 18 is the Raman spectra of the Cellulose acetate and 17.5%w/v PVP-CA composite functional groups.

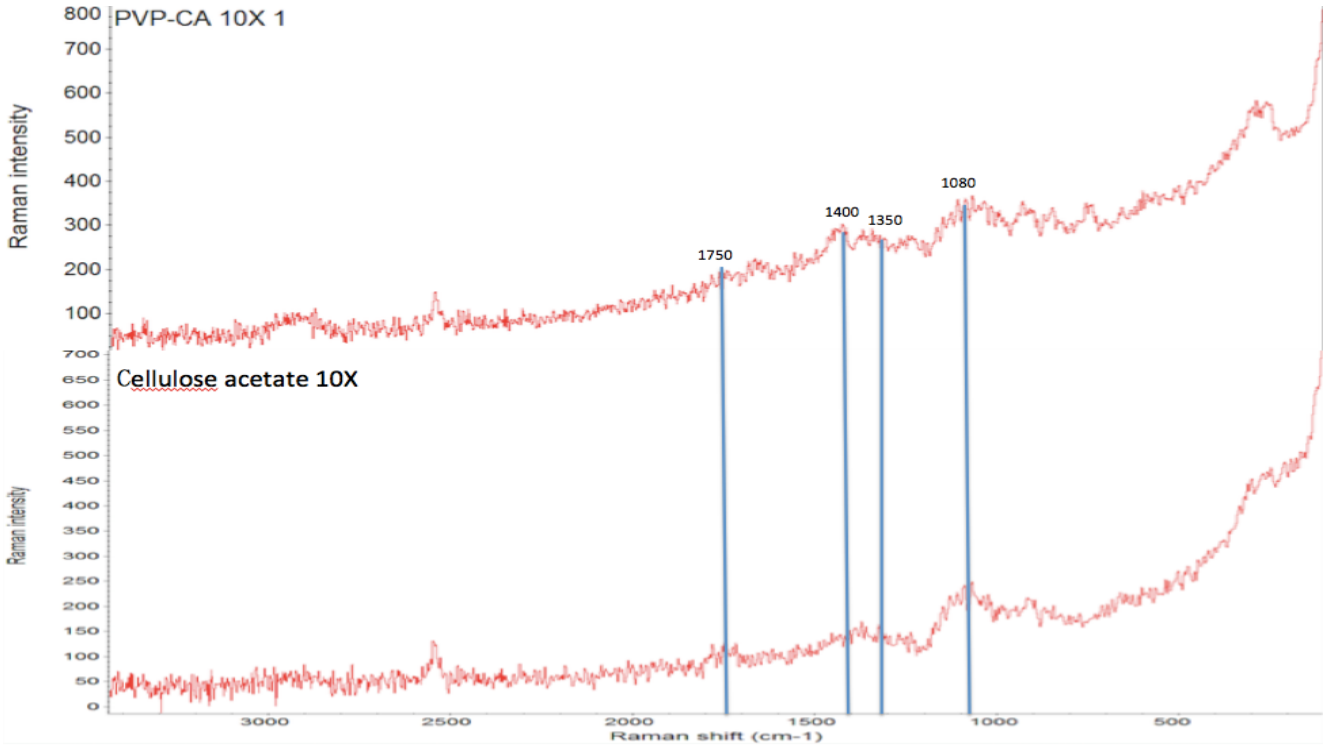


Figure 18: Raman spectra of CA and PVP-CA composite

In figure 18, the Raman spectrum of pure CA shows a broad band in 1750cm^{-1}, which is the carbonyl group: C=O stretch. And for the peak in 1080cm^{-1}, it is the ester groups stretch. Both of these groups became weaker in PVP-CA composite. It is attribute to the Hydrogen bonding formatted between PVP and CA. What's more, the band in 1350cm^{-1} is the OH in-plane bond. It is also less pronounced in PVP-CA spectra. This peak is really small because O-H stretch is not obvious in Raman spectrum. The decrease of this peak should be the same reason, the formation of intermolecular hydrogen bonding.

On the other side, the peak located at 1400cm^{-1} in PVP-CA composite responded to the C-N group vibration. The presence of this small peak proved the existence of PVP component.

3.2 Hydrophilic and Oleophilic test analysis

2-layer fibers and 17.5%w/v composites have been chosen to do the test. Figure 19 is the samples before test. Figure 20 and 21 are the hydrophilic test. Figure 22 is the picture of oleophilic test.

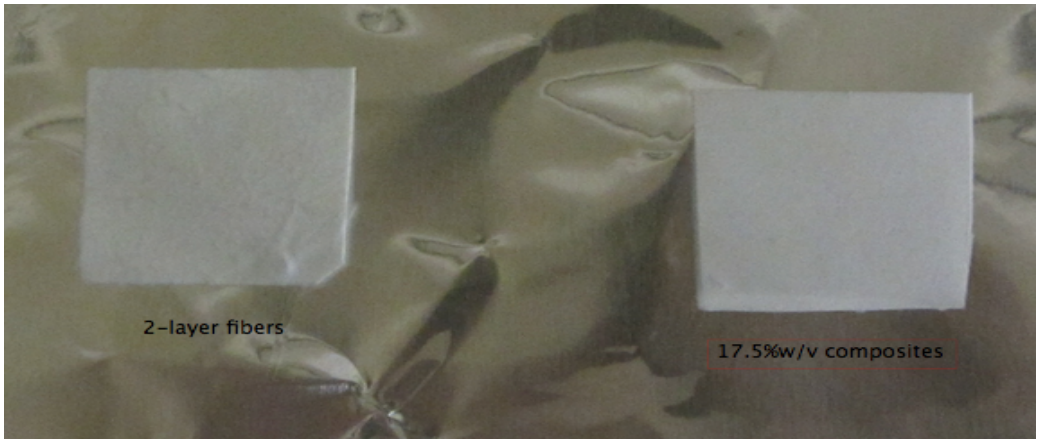


Figure 19*: Fibers before test*

Figure 20*: 1 min after hydrophilic and hydrophobic test*

Figure 21*: 3 min after hydrophobic and hydrophilic test*

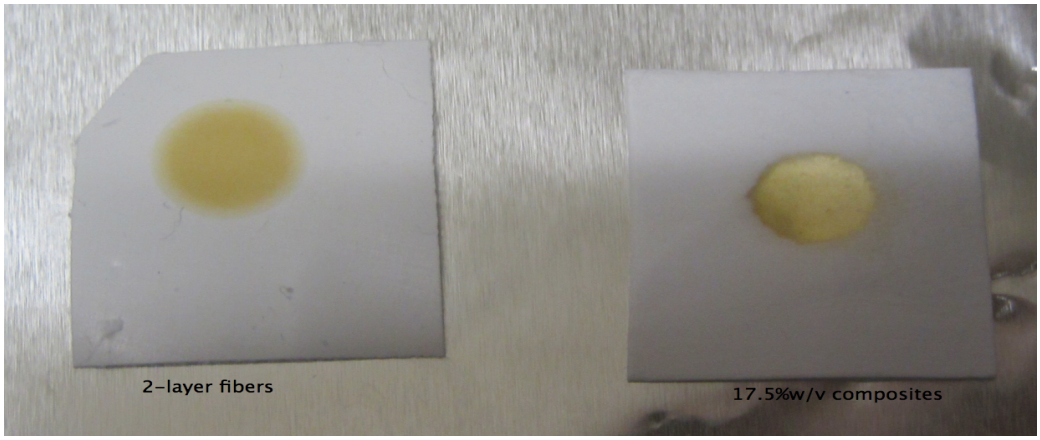


Figure 22*: Fibers after Oleophilic test*

Obviously, figure 22 showed that both 2-layer fibers and PVP-CA composites were lipophilic.

From Figure 20 and 21, 17.5%w/v composites were obviously hydrophilic. However, for the 2-layer fibers, we tested the CA layer because PVP layer would be absolutely hydrophilic. After one minute, CA fibers were hydrophobic, but 3 minute later, one drop of water started to dissolve. The other one still didn't dissolve. That meant CA fibers appeared like hydrophobic for a while.

Figure 23 explains the mechanisim of this phenomenon. Since CA surface is a rough surface, each CA electrospun fiber has contact angel to the water. The contact angel between water and CA rough surface should be bigger than 90 °. That's why the water drops can stay on the CA surface, not absorbed

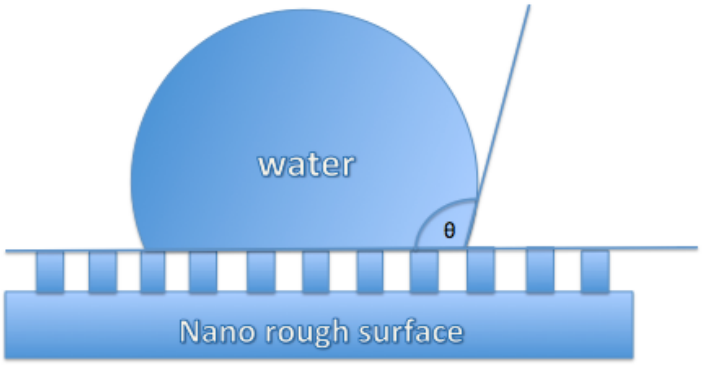


Figure 23*: mechanism of hydrophobic phenomenon.*

3.3 Oil absorption test analysis

Firstly, figure 24 and 25 are the images of 10%w/v and 17.5%w/v composite before and after oil absorption. 20ml No.6 oil was poured into 250ml beaker. 4 pieces 3cm*3cm fibers for both 10%w/v and 17.5%w/v composites were prepared. Each piece of fiber immersed into the oil one by one, then picked up from the beaker and waiting for 2 min, then weighed by the machine. The data of the fibers' weight before and after test were showed in table 5:

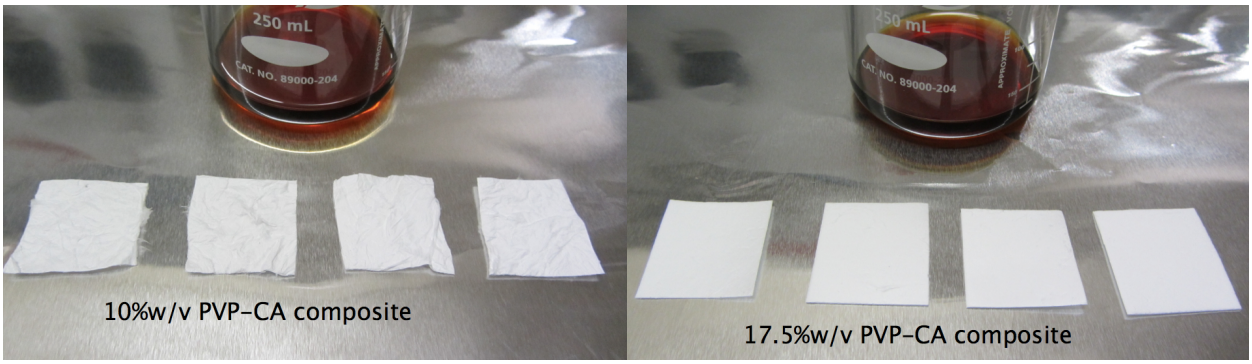


Figure 24*: 10%w/v, 17.5%w/v PVP-CA composite (Before absorption)*

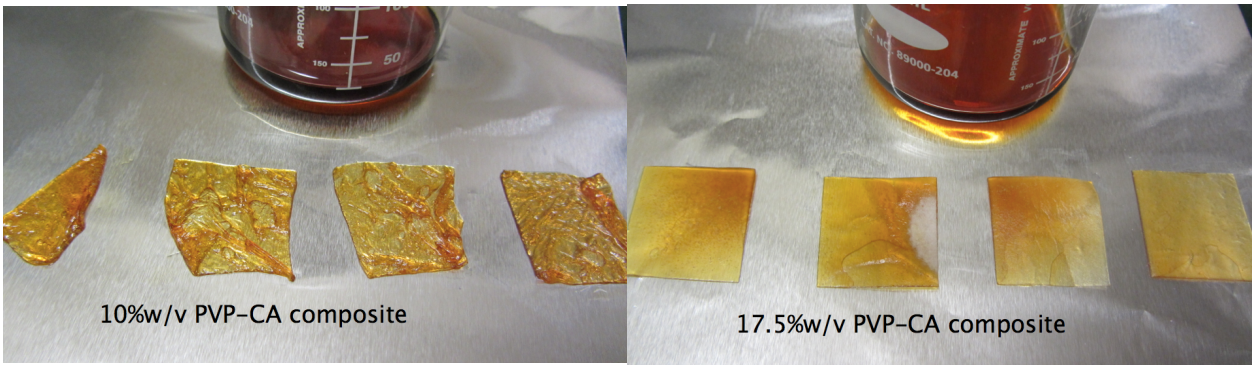


Figure 25*: 10%w/v, 17.5%w/v PVP-CA composite (After absorption)*

Table 5: No.6 oil absorption data 1:

No.6 oil absorption					
10%w/v PVP-CA Composite					
	Before (w1)	After (w2)	w2-w1	(w2-w1)/w1	Average of (w2-w1)/w1
1	0.0167	0.3746	0.3579	21.4311	22.0979
2	0.0247	0.5528	0.5281	21.3806	
3	0.0190	0.4625	0.4435	23.3421	
4	0.0244	0.5670	0.5426	22.2377	
17.5%w/v PVP-CA Composite					

1	0.0775	0.4856	0.4081	5.2658	5.0285
2	0.1036	0.5970	0.4934	4.7625	
3	0.0763	0.4773	0.401	5.2556	
4	0.1259	0.7340	0.6081	4.8300	

From table 5, w1 is the weight of fibers before test and w2 is the weight after oil absorption. (w2-w1)/w1 is the relative oil absorb weight of fibers, which is important for an oil absorption material. This value for 10%w/v composite is as high as 22, means 1g fibers can adsorb 22g oil. However, for 17.5%w/v composite, the value is only 5.0285. In my opinion, the reason is that 10%w/v composite has much smaller fiber diameter and distance between fibers is also smaller than 17.5%w/v, so the smaller fibers and non-woven structure kept much more oil than 17.5%w/v composite.

Then figure 26 and 27 are images about oil and oil-water absorption for 2-layer fibers and 17.5%w/v composite. 2*20ml No.6 oil were poured into two 250 ml beakers, one with water, the other one without water. 4 pieces 3cm*3cm fibers of each sample were prepared for the test. Then same procedure was used as 10% and 17.5%w/v fiber oil absorbance test. Table 6 shows the data of both 2-layer fibers and 17.5%w/v composite oil absorption test:

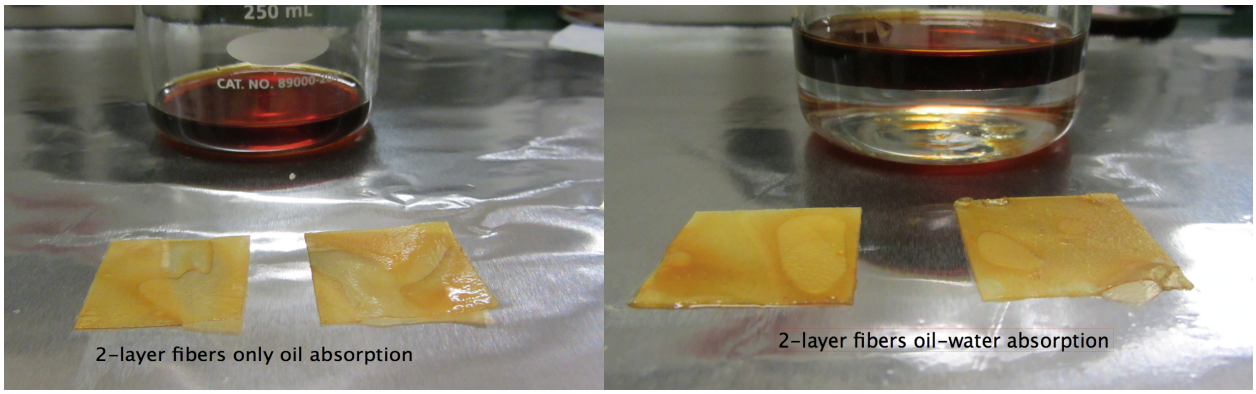


Figure 26*: 2-layer fibers only oil and oil-water absorbance test*

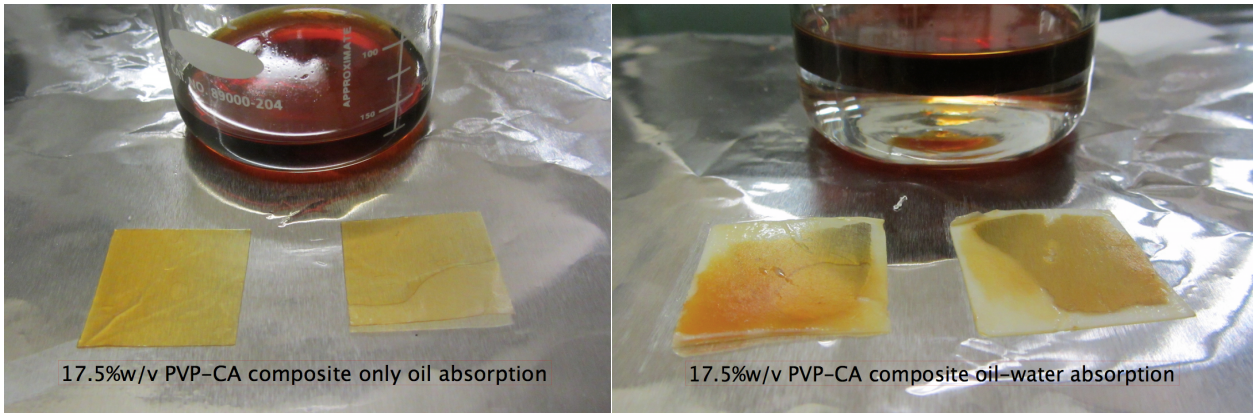


Figure 27*: 17.5%w/v composite only oil and oil-water absorbance test.*

Table 6: No.6 oil absorption data 2

No.6 oil					
Only oil					
17.5%w/v composite	Before(w1)	After(w2)	w1-w2	(w1-w2)/w1	Average of (w1-w2)/w1
1	0.524	0.3610	0.3086	5.889	5.675
2	0.421	0.2720	0.2299	5.461	
2-layer fibers					
1	0.0888	0.3320	0.2432	2.739	2.7325

2	0.1006	0.3749	0.2743	2.726	
Oil-water					
17.5%w/v composite	Before(w1)	After(w2)	W1-w2	(w1-w2)/w1	Average of (w1-w2)/w1
1	0.0492	0.3757	3.3265	6.636	6.0625
2	0.0900	0.5840	0.4940	5.489	
2-layer fibers					
1	0.1054	0.4666	0.3612	3.427	3.0755
2	0.1016	0.3865	0.2849	2.804	

In table 6, as same as table 6, the most important value is (w2-w2)/w1. This value for 17.5% composite is 2 times higher than 2-layer fibers. Which means 17.5% composite adsorbed double weight of oil compared with 2-layer fibers. Since these two kind of electrospun fibers have same component: PVP and CA. Thus the reason for this should be the intermolecular reactions between PVP and CA in the composite. The formation of hydrogen bond between PVP and CA in acetic acid and acetone solvent might help the oil absorbance ability for the PVP-CA composite.

3.4 Discussion

In this work, PVP-CA composite was successfully prepared as electrospun nanofibers. Since the acidic environment may induce the hydrogen bonding[3], the acetate acid was chosen as solvent for PVP and CA composite. Acetone was used too because it was a good solvent for CA. PVP was used to modify bacteria cellulose because the presence of both C-N and C=O could

provide more electron to absorb Ca^{2+}, then easier to combine CO_3^{2-} and PO_4^{3-} in hydroxyapatite[21].

Different electrospinning parameters were used to make the PVP and CA composite because different voltage, flow rate, and concentration can affect the diameter and distribution of the fibers[9] Besides, some other parameters, like the temperature and humidity also would influence the structure of electrospun fibers.

Table 6 and table 7 are oil absorbance data for the electrospun fibers. But in table 5, the relative oil absorbance weight for 17.5%w/v composite is a little lower than that in table 6. In my opinion, the reason should be the moisture effects. Data in table 5 were collected 3 days later than table 6. Since during those days, the whether is humid, the composite fibers were absolutely absorbed some water in the environment. Then the fibers' oil absorption capacity had been affected.

Some other factors, like the thickenss of the sample would influence the oil absorbance too. Since some electrospun fibers I took from the center of the collector, some were from the edge of the collector. Thus the central samples were thicker than others. It is possible thicker samples absorbed less oil than thinner ones due to the lower specific surface area to the oil than the thinner samples.

2-layer fibers, each single fiber and 25% PVP in water electrospun fibers were made as control groups. Of course, some characteristics of them had been discussed too.

CHAPTER 4: CONCLUSION

By employing the elctrospinning technique with various operation parameters, the 7.5%, 10% and 17.5%w/v PVP-CA composite fibers were successfully manufactured using acetic acid and acetone as solvents. As the comparison, single layer of PVP/water and CA/acetone solutions electrospun fibers and PVP-CA two-layer electrospun fibers were produced. SEM images showed the surface structure and the diameter of all above electrospun fibers. Raman spectroscopy test proved the existence of intermolecular reaction: the formation of hydrogen bond occurred between PVP and CA in the solutions. Then the oil absorption ability was tested for the fibers. The weight of 10%, 17.5%w/v composites, two-layer fibers before and after immerged into the No.6 oil was recorded. From the results, 10%w/v composite fibers had the best oil absorbance ability however two-layer fibers were the worst. This concludes PVP-CA composite fibers that with lowest weight/volume concentration exhibited the most excellent absorbance ability than both of other concentration composites and the two-layer fibers.

CHAPTER 5: FUTURE WORK

Many works have been done about PVP and CA composites. Some used electrospinning technique to prepare it, some focused on the phase inversion method. Both PVP and CA are important polymers due to their excellent properties. For the PVP and CA composite membranes, many other works can be done in the future, like the mechanical test and the FTIR test. The mechanical test can tell us the strength of composite fibers, which is really important for its further application.

In the application field, it can be used in many other fields except the oil-absorption. Some people treated it as drug release scaffold, so the drug release time had been collected; some used the composite membrane for ultrafiltration of metal ion. I believe the strength and cheap polymer PVP and biocompatible polymer CA will attract much more scientists' attention in the future.

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