Lab 1: PAN/PVA Nanofiber Electrospinning Fabrication and Post-annealing

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for
MSE 60: Advanced Laboratory in Synthesis and Characterization of Materials

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ABSTRACT *(Kelsey Lawson)*

Polymer solutions, polyacrylonitrile (PAN) in N, N-Dimethylformamide (DMF), and polyvinyl alcohol (PVA) in DI water were prepared to undergo a technique to produce polymer fibers, called electrospinning. This process was completed under room temperature conditions to form fiber mats of each polymer respectively. Once formed, each polymer sample was oxidized in compressed air then annealed in H2N2 gas. The samples prior to each stage were imaged under a scanning electron microscope, SEM. From the images, it was estimated that the oxidation and annealing process had affected the PVA samples the most. Compared to the spun sample images, after treatment, the PVA fiber diameter increased, both textures of the fiber and surface roughened, and the structure of the fiber placement changed from a woven pattern with visible gaps to one uniform mass with overlapping fiber. Although the PAN sample after treatment didn't experience a drastic transformation like PVA, it still resulted in smaller fiber diameters and had shifted its uniaxial direction to a perpendicular staircase overlap. TGA, DSC, and Raman plots were conducted and analyzed for each polymer under each categorical condition. From the TGA both PVA and PAN had a loss of mass however PVA was characterized as multistage decomposition and PAN's two significant curves are a single-stage decomposition and product decomposition. Yet, on the DSC plot, both PVA and PAN continued similar trends of endothermic reactions but PVA had a higher heat flow estimated at 250 mv compared with PAN at 120 mv. Finally, the three systems of each polymer were analyzed under a Raman plot concluding that: PAN at room temperature and PVA at room temperature are considered cyclic graphitic carbon whereas PAN oxidized at 250℃, PAN annealed at 1000℃, PVA oxidized at 215℃ and PVA annealed at 800℃ are considered disordered carbon.

INTRODUCTION *(Kelsey Lawson)*

Electrospinning is the process of using electrostatic forces to produce polymer fibers at the nanometer diameter (1). This is achieved by inducing charges through an electric field to then create tensile forces that pull the polymer fluid in the axial direction of their flow creating these thin fibers (1). When the electrical field is increased, the tip of the capillary tube where either a polymer solution mixed with a solvent, or polymer melts, are held in the form of a conical shape known as the Taylor Cone (2). A critical value has to be met for the electrostatic force to overcome this surface tension at the tube because it creates the charged jet of fluid polymer to eject in a single stream to be collected (2). The distance traveled for these polymers lets the solvent evaporate leaving the thinly stretched fiber (2) to collect on an oppositely charged substrate represented by a stationary flat plate or rotating drum (1). At the substrate, each fiber is stacked on previously drawn fibers creating a mat to then be processed under a form of microscopy, such as scanning electron microscopes (SEM). Through examination, electrospun polymer nanofibers have attracted the attention of materials research because of their enhanced thermal and mechanical properties compared with their counterparts of regular fibers and bulk polymers (1).

Within this technique, there are multiple parameters to affect the outcome of how the nanofibers are produced and what properties are exhibited. Haung (2003) investigated these various parameters and how they can transform the fibers from the polymer solution during electrospinning. The top three categories mentioned are as follows: (1) the solution properties such as viscosity, elasticity, conductivity, and surface tension (2) governing variables such as hydrostatic pressure in the capillary tube, the electric potential at the capillary tip, and the distance between the tip and the collecting screen (3) ambient parameters such as solution temperature, humidity, and air velocity in the electrospinning chamber (3). By adjusting one or all of the parameters in each category, researchers can strategically develop new methods of producing nanofibers.

A common application for electrospun nanofibers is to create carbon and graphitic nanofibers for storage cells (1). Because of the enhancement in mechanical properties, these nanofibers are used as fillers reinforced composites increasing stiffness, high strength, and low electrical resistivity (1). The way these fibers are collected, as aligned or random, can affect what properties they have (1). For example, aligned fibers offer higher mechanical properties than the randomly aligned fibers due to the compressive and torsional abilities (1). This application is one of the many ways electrospun nanofibers can be used to improve existing systems and why it is a growing field.

Moreover, the lab conducted and discussed in this paper, involves two polymers, polyacrylonitrile (PAN) and polyvinyl alcohol (PVA) are prepared as a polymer solution with their respective solvents. This solution is the polymer fluid to be electrospun providing the base to conduct experiments under oxidation and annealing processes. Throughout this experiment, at each interval between electrospinning, oxidation and annealing, scanning electron microscopy (SEM) images are taken and analyzed within the report. Furthermore, TGA, DSC and Raman curves are plotted using the data provided from the lab. The results from these plots are discussed explaining how each polymer reacted in both instances to oxidation under compressed air and in the H2N2 gas. Because the polymers have different thermal stability levels, PVA is tested at lower temperatures for the heat treatments than PAN. This is examined further in the report.

OBJECTIVE *(Keven Colchado)*

The polymer lab will utilize the electrospinner to create polymer material that would then be going through the annealing process. The purpose of the lab is to identify the different characterization of each polymer sample. There should be a distinguishable difference between PAN and PVA mat and oxidized and non-oxidized materials.

MATERIALS AND EXPERIMENTAL METHODS *(Keven Colchado)*

Materials

1.2 g Polyacrylonitrile (PAN)	1.2 g Poly(vinyl alcohol) (PVA)	8.8 g N,N-Dimethylformamide
Spatula	8.8 g H2O Solution	Gas tubes
Mineral Oil	1000 ml Beaker	Weight Paper
Tweezer	Crucible	Electronic Scale
Syringe (x2)	Electrospinner	Tape
2 Aluminum foil size 12x4 inches	Tray Cart with cover and trays	Gas Cylinder with compressed Air
2 Glass Vials with caps	Heat Plate	Pipette
250 ml beaker	2 Stir bars	Aluminum Specimen mounts
Fume Hood	Flow Meter	Tube Furnace
Scanning Electron Microscope	Metal Rod	Storage tube
2 Capsule	Label Tape	Carbon Tape (Pelco Tabs)
Razor Blade	Sputter Coaster ACE200 (Leica)	SEM Microscope
Screwdriver	Pressing Rod	Thermogravimetric Analyzer
Glass Slide	Raman Laser (785nm)	Optical Microscope

Experimental Methods

Before the electrospinning lab, wear the proper PPE. There would be hazardous material involved. You will need to use splash goggles, nitrile gloves, and a lab coat.

Electrospinning Lab

Clean a spatula with wiping paper. Fold a weight paper diagonally. Place the weight paper on the electronic scale then calculate the weight. With the spatula, pour the PVA on the weighted paper that is on the scale. Pour until the scale reads 1.2 g plus the weight of the weighted paper. Then set aside the weighted paper with PVA. Repeat weighing process with PAN instead of PVA. Clean the scale and the work area. Under a fume hood place an open glass vial on scale. Calibrate the scale with the glass vial. Pour in PAN from the weighted paper to the glass vial. With a pipette, pour N,N-Dimethylformamide into the vial slowly until the scale reads approximately 10g. Then remove the solution from scale. Place a new glass vial on the scale. Calibrate the scale with the vial. Pour PVA solution from the weighted paper into the vial. Pour H2O solution into the vial until the scale reads 10g. Then remove the solution from scale. Under the fume hood, place a stir bar inside the PVA solution and another stir bar in the PAN solution. Close both vials. Place both solutions on their own heat plate. Set plates to 100 rpm and 80oC for 8 hours. After 8 hours, reduce heat to room temperature for 12 hours. Turn off the heat plate and set solutions aside. On a workbench, cut two pieces of 12x4 inch aluminum with scissors.

Turn on the electrospinner. Set voltage to zero then open the electrospinner and tape one aluminum 12x4 on the roller with the shorter side being parallel to the roller. Under the fume hood, open the PAN solution vial. With a syringe, take out about 2-3 mL of the solution. Place the syringe on a surface with the needle facing upward. Allow the bubbles in the syringe to rise up until a big bubble is formed. Once the bubbles merge, slowly squeeze out the bubble from the syringe and wipe clean the needle carefully. Place some paper towels on the surface of the electrospinner. Place the syringe in the intruder and tighten it up. Close the electrospinner and lock it. Turn on the light of the electrospinner. On the panel, click Pump 1 and set the injection rate 0.6mL/hr. Set the roller to rate 1500 rpm. Set the voltage on the right side to -5V and +10V on the left side of the electrospinner. Allow the process to occur for an hour and twenty minutes. Adjust voltages on both sides to zero, stop the roller and injection rate. Open the electrospinner and remove the aluminum with a sample off the roller. Place the sample on a tray, with the mat facing up, then place it on the tray cart. Clean the electro spinner and replace the paper towels. Repeat steps involving syringe, setting up and using electrospinner with PVA solution instead of PAN. Then turn off the electrospinner. Leave trays on sample overnight.

Cut samples of PAN fiber mat small enough to fit on a crucible. Pull the mat from the aluminum foil using tweezers. Place extracted mats in the crucible, stacking mats on top of each other. Stack 7-8 layers. Begin setting up the tube furnace by first attaching a tube of compressed air to a flowmeter and a tube between the flowmeter and the tube furnace. Lock the tubes in place. Open the tube furnace and estimate the location of the larger heating filament from the end of the tube by using a rod. Tape the rod where it meets the end of the tube. Close the tube furnace. Place the crucible with PAN fibers in the tube and push the inside with the metal rod until the tape of the rod matches the end of the tube. Close the end of the tube with its valve. Attach a tube to the valve into a beaker filled with mineral oil. This is so there is a consistent flow and no gas dissipates. Open up the cylinders of compressed air until it reaches 100 cc/min on the flowmeter. Turn on the tube furnace and set the temperature to 250oC with a ramp rate of 5oC/min. Hold for 4 hours at 250oC then let it cool naturally for eight hours. Turn off gas. Remove crucible with samples. Record observation. Leave some samples on the crucible and place the crucible back inside the tube furnace. The rest of the sample, placed inside a capsule and labeled “PAN Oxidation.” Reattach pieces of tube furnace back together. Detach the cylinder of compressed air and attach the cylinder with 5%H2 and 95%N2 gas. Open the gas cylinder until the flow meter reads 100cc/min. Turn on tube Furnace and set the temperature to 1000oC into a ramp rate of 5oC/min. Hold at 1000oC for an hour then let cool naturally for eight hours. Turn off the gas and remove samples from the tube furnace. Record observations. Place samples in a capsule and label “PAN carbonization.” Then clean up. Repeat processes using tube furnaces with PVA samples instead of PAN. For the oxidation process, set the temperature to 215oC for 2 hours. For the carbonization process, set the temperature to 800oC for an hour. Label capsules appropriately.

Characterization Lab

Attach aluminum mount to storage tube then attach a carbon tape on the aluminum mount with tweezers. Cut small samples of aluminum foil. Samples will need to be small enough to fit the carbon tape. Repeat these steps using PAN oxidation, PAN carbonization, PVA oxidation, and PVA carbonization samples. Cut samples using a clean razor blade. Make sure to clean the blade after each cut. One aluminum mount should have aluminum cut and both PAN samples. A second aluminum mount will have an aluminum cut with both PVA samples. Close storage tubes when done. You will then program the electron sputter (Leica) using platinum and palladium layers and pump to 4 nm thickness. This process is used in order to give a charge to the polymer samples. Then turn on the SEM equipment. Allow the equipment to complete its venting. Once done, open the SEM chamber. Then open the storage tube with PAN and place each sample into a sample cavity in the chamber. Screw in the chamber and close the SEM chamber and turn on the vacuum. This is necessary so that the samples stay in place. When complete, adjust the contrast and brightness of the image in order to make it clearer. Slowly adjust the distance of the microscope and samples to 5 mm. Then proceed to adjust magnification until the fibers are clear on the screen. Record any observation of the sample. Save any images of the sample that will be used for observation. Repeat observation to each the samples on the mount. Once done, click home position to return the pedestal to return to original position. Then remove the sample and repeat steps for PVA samples.

Using leftover PVA and PAN from the electrospinner lab that was not oxidized, weight each sample. First you will need to calibrate an electron scale with a clean crucible. On weight paper, cut a piece of PVA mat and condense it together using a clean metal rod. Make sure to use about 14 mg of the sample. Repeat using the PAN sample. Turn on the Raman spectrometer. Input the PVA weight sample in the spectrometer and make the environment inside to be air with 50mL/min air flow. Place the sample inside and close the chamber. Turn on the program and allow the spectrometer to calculate the data. Remove the sample once the process has been completed. Repeat process using PVA sample. Then place each different sample of PVA and PAN mats on a glass slide. Make sure to label each sample. Place the slide on an optical microscope with a Raman laser. The laser will need to be 785nm with 1% intensity. Allow the laser to acquire data for twenty seconds on each sample. Clean up and dispose of samples appropriately.

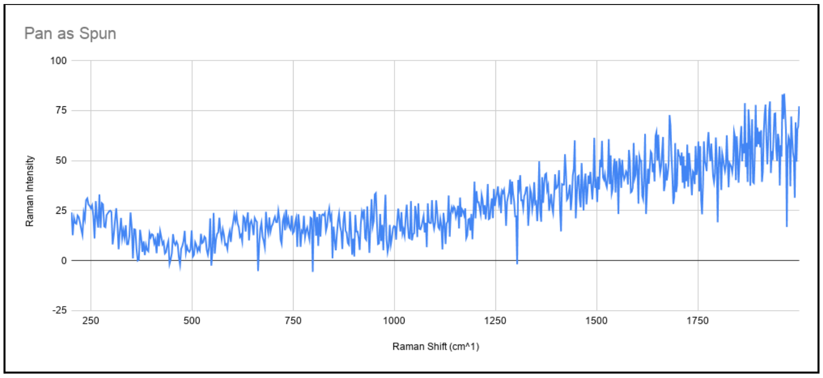
RESULTS *(Thaily Serrano-Alamo)*

SEM Images

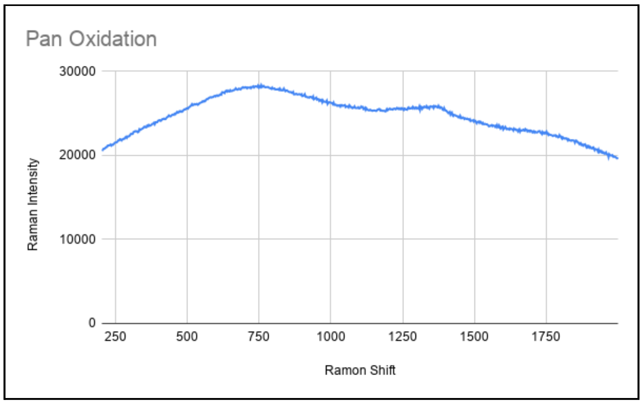
See Appendix

Raman Spectra

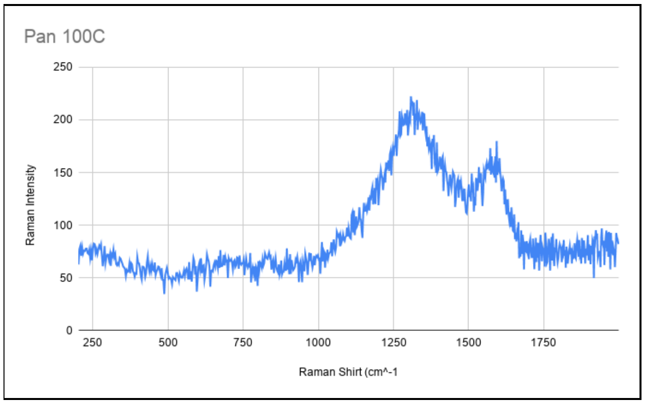
Graph 1. (There's a lot of peaks so close to each other that it hard to identify the peaks.)



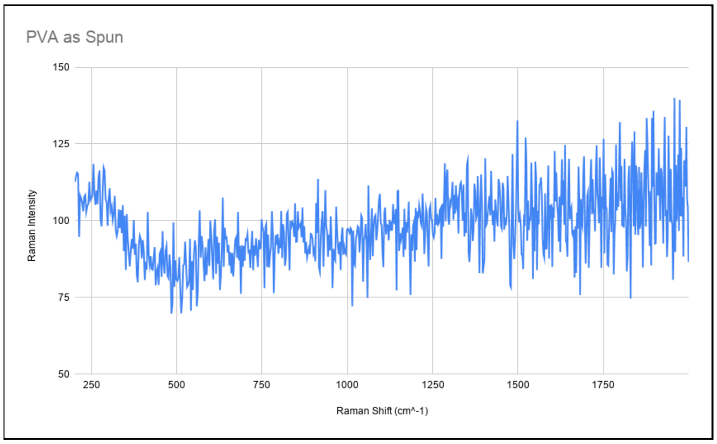
Graph 2. (There are no steep peaks. It seem like there is two wide peaks at around 750 cm^-1 and 1,375 cm^-1)



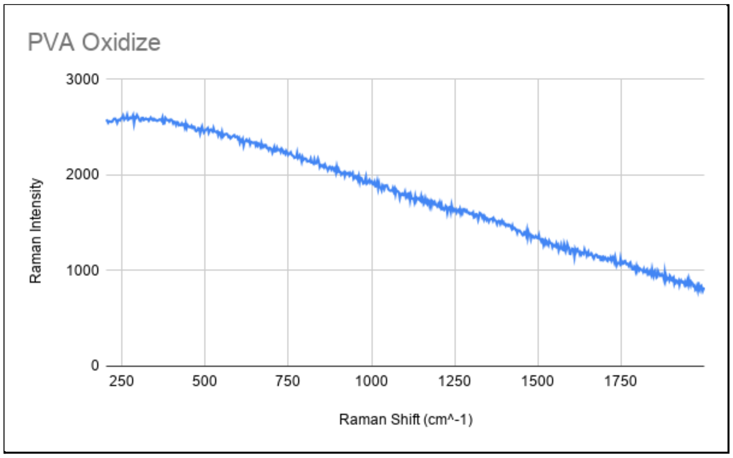
Graph 3. (There are two steep peaks at 1,300 cm^-1 and 1,600 cm^-1)



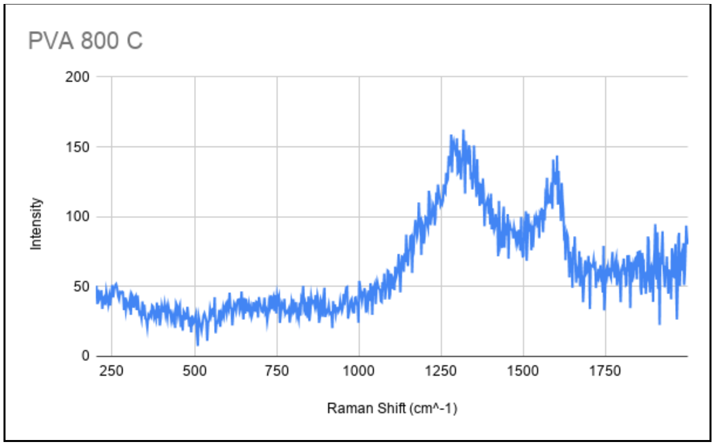
Graph 4. There are a lot peaks so close together that it is hard to identify the peaks.



Graph 5. The graph looks like it is decreasing at a constant rate, unlike the other graphs. It does not seem like there is a peak.

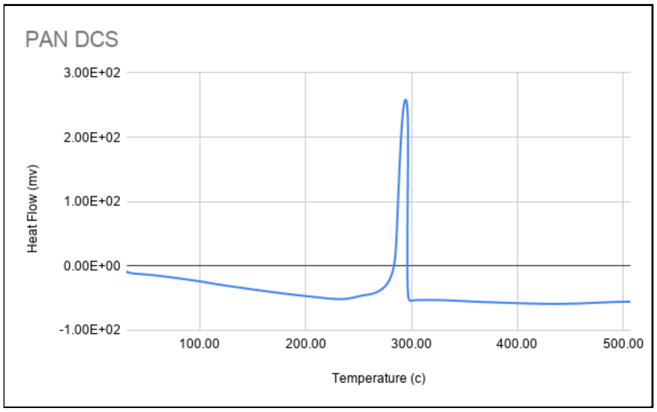


Graph 6. Two peaks at 1,300 cm^-1 and 1,600 cm^-1

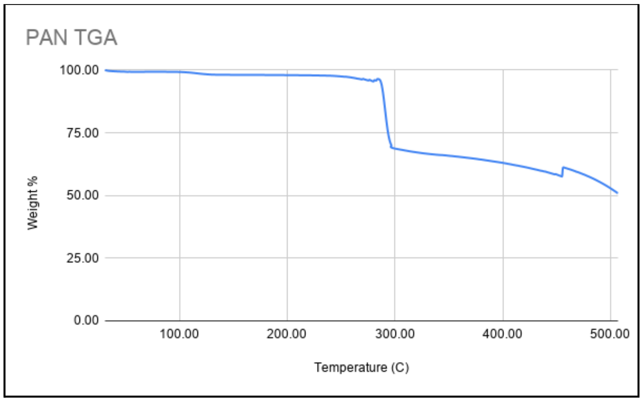


PAN TGA & DSC CURVES

Graph 7. The peak is at about 290 C. For most of the graph the heat flow is decreasing.

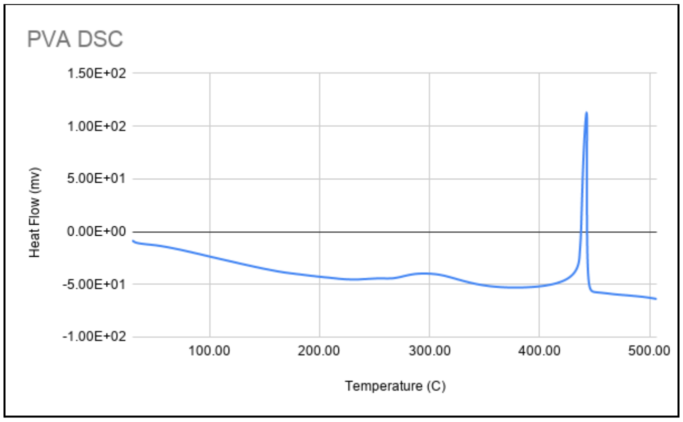


Graph 8. The weight percentage starts in 100 % but does not end in 0 %. It does keep the basic shape of a TGA graph. T i is about 290 C and T f is about 500 C.

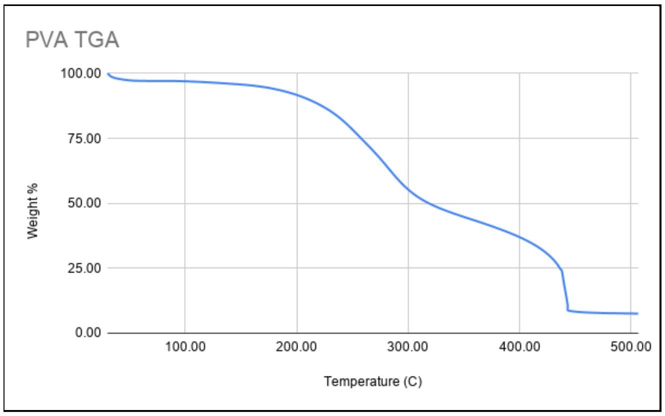


PVA TGA & DSC CURVES

Graph 9. For most of the graph, heat flow is decreasing as temperature is increasing. Until the peak, around 440 C.



Graph 10. T_i is about 250 C and T_f is about 450 C . This weight percentage starts at 100% and ends at about 7%, almost 0.



DISCUSSION *(Kelsey Lawson)*

In the lab, both polymer precursors, polyacrylonitrile (PAN) and polyvinyl alcohol (PVA) were prepared as a polymer solution to be electrospun. The type of solvent used for each polymer differed: 12 wt% of PAN in N, N-Dimethylformamide (DMF), and 12 wt% of PVA in DI water. Both polymers utilized the same parameters for electrospinning so that each sample was initially spun at room temperature. In Figures 1 and 2, the SEM images of these spun fibers can be seen. Comparing the 200 μm images for both PAN and PVA, the PAN sample is more fibrous due to each layer of nanofiber being visible whereas in PVA it resembles a solid surface.

As the magnification increases for the PVA sample from 400 to 1µm, the surface starts to break down into each nanofiber revealing that they are all compacted in various directions each ranging in diameter thicknesses. This can be seen in the 40 µm image at the earliest however, both the 20 µm and 1 µm magnify the detail of the woven pattern of the fibers and the smooth texture. Although each PVA's fiber diameter varies in the 1 µm image, it can be estimated that they range from a quarter to less than half of a micron. This is unlike PAN, where the lowest magnification image at 400 µm shows the fibers spaced out, and in the 200 µm, individual fibers can be identified with uniform diameters. Increasing the magnification from 20 to 1 µm for PAN, the uniformity of the fibers is confirmed and an individual fiber's texture is shown to be bumpy. The size of the fiber shown in the 2 µm image can be estimated at 1-micron diameter and can be confidently applied to the others not shown due to the unique consistency, unlike PVA. Although the PAN sample shows homogeneity along with each fiber and with each diameter, there is any inconsistency between the fibers and depending on the viewing angle, can vary the number of fibers seen. This is the opposite in PVA showing true spatial homogeneity because of the densely packed fibers, yet as mentioned previously, there is no consistent diameter or along each fiber showing impurities within the pattern as seen in Figure 1a in the middle top. Relating the lab results to a research article by Belyaeva (2013), the oxidation of PAN results in the destruction and restructuring of the fibers that are originally linear into a more complex staircase pattern (4) which is confirmed in Figure 3c.

The next step is to oxidize each spun sample in air and annealed in a forming gas, H2N2, yet PVA is oxidized at a lower temperature due to its thermal instability compared to PAN. In Figures 3 and 4, PAN samples were oxidized in compressed air for 4 hours at 250℃ and then annealed in H2N2 for 1 hour at 1000℃ yet don't show as much change to the original spun sample. Yet, comparing Figure 1a with Figures 3a and 4a, it seems that under oxidation the PAN fibers have shrunk and become more disorganized in fiber orientation. Whereas the PVA samples oxidized in compressed air for 2 hours at 215℃ then annealed in H2N2 for 1 hour at 800℃ completely changed structure by losing the gaps between the woven fibers and becoming entangled with neighboring fibers. Even the woven pattern found in Figure 2 has reduced down and is no longer visible, instead, the fibers have merged to form a bark-like textured surface both in low and high magnification images. Even the fiber texture has changed into a rougher exterior unlike in Figure 2a. Opposite to PAN, it seems that PVA under oxidation increases fiber diameter as well as impurity content because of the shift in a denser structure. Regarding PVA, a similar study by Senkevich (2006) used an aqueous PVA solution to undergo thermal oxidation in 200℃ for 16 hours in compressed air resulted in partial dehydration of PVA led to the formation of carbon structures (5) explaining the newly rough surface after oxidation.

In the results, TGA and DSC graphs were plotted for both PVA and PAN. The TGA graph is an analysis of the data provided to resemble the mass loss of the reaction of the polymer’s energy from the system. Within the TGA graph for PVA, there are two significant downward humps with the first one estimating at 250℃ then the second one around 380℃. The humps are characterized as a multistage decomposition of PVA’s mass at the specific temperatures estimated. For the PAN TGA graph, the curve is hostile with a sharp downward direction around 290℃ then a little blip upwards around 450℃. The first slope is characterized as a single-stage decomposition whereas the second slope is product decomposition at higher temperatures. Next, the DSC graph is to represent the differential scanning calorimeter or the difference in energy between a reference temperature and the actual temperature accounting for system changes such as glass transition and exothermic or endothermic reactions. For PVA, there is a massive upwards spike around 440℃ estimating a heat flow of 250 mv predicting a thermal melt, or endothermic reaction absorbing heat. The same can be inferred for PAN except at around 390℃ estimating 120 mv.

Another graph is the Raman Spectra that is best for molecules that are not already dipoles, to see how crystallized the carbon will be in the polymer. To analyze the data in the results, a range for the curves correspond to the carbon being disordered, low values, or cyclized graphitic, high values. Going in the order of the graphs listed in the results section: PAN at room temperature is sloped towards the higher end making it more cyclized graphitic carbon; PAN at 250°C is sloped higher on the low-value side making it more disordered carbon; PAN at 1000℃ is also slowed towards the lower values and would be considered more disordered carbon; PVA room temperature is leaning towards the higher values making it cyclized graphitic carbon; PVA at 215℃ is heavy on the low-value side making it disordered carbon; PVA at 800℃ is close but has a higher peak in the lower value making it disordered carbon.

CONCLUSION *(Thaily Serrano-Alamo)*

Polyacrylonitrile (PAN) and Polyvinylalcohol (PVA) were prepared with their solvent solution to produce electrospinning under two processes, oxidation and annealing. Before each step the samples were analysed under SEM to see the diameter of the fibers. Then TGA, DSC and Raman were performed for each stage.

The SEM images showed us the difference between PAN and PVA. At room temperature PAN has more inconsistency in fiber diameter while PVA has a is more homogeneous. After oxidation, PVA increased it’s fiber diameters and PAN’s fibers decreased. The TGA graphs showed that both PVA and PAN are endothermic reactions absorbing heat. Except their thermal melts are at different temperatures. For PVA it is at 440 C and PAN is at 390 C. Lastly the

Raman shift graphs shows how crystalised the carbon is. On average, both PAN and PVA in room temperature have higher slopes so it is more crystalized. PAN at 250 C and PVA at 215 C, are disordered. PAN at 1000 C and PVA at 800 C are more disordered.

References

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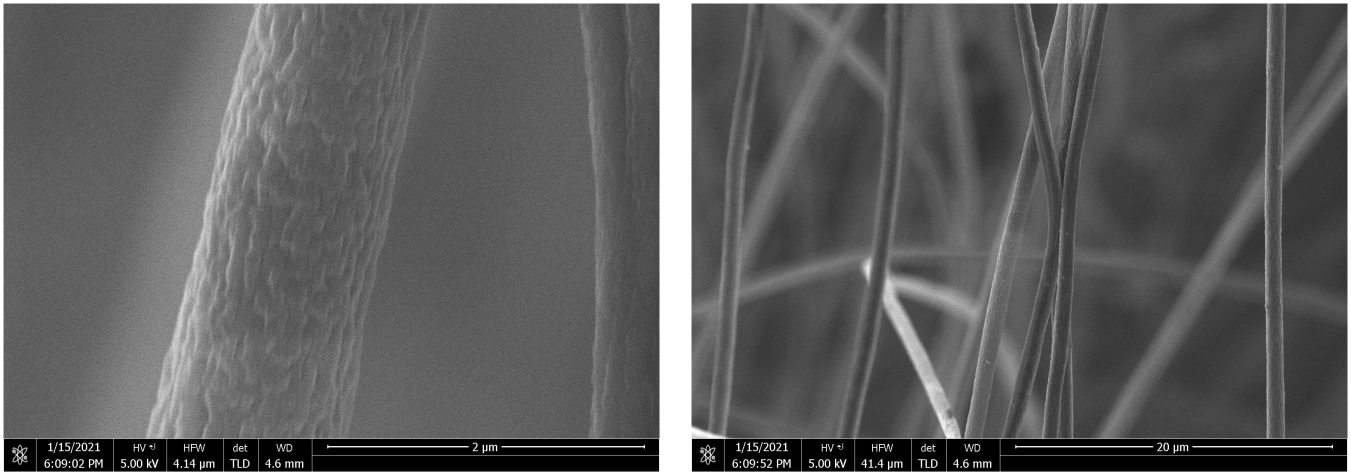
Appendix *(Kelsey Lawson)*

Figure 1. Shown below are SEM images of air spun PAN. The order from (a) through (d) scales down in magnification. Both (c) and (d) have similar fiber construction and only when referencing (a) and (b) can it be revealed that the individual fibers have uniform diameters, are textured, and there is the random spacing between each fiber yet maintains a general direction.

a) 2 µm, WD 4.6 mm

b) 20 µm, WD 4.6 mm



c) 200 µm, WD 4.4 mm at 500x

d) 400 µm, WD 4.4 mm at 250x

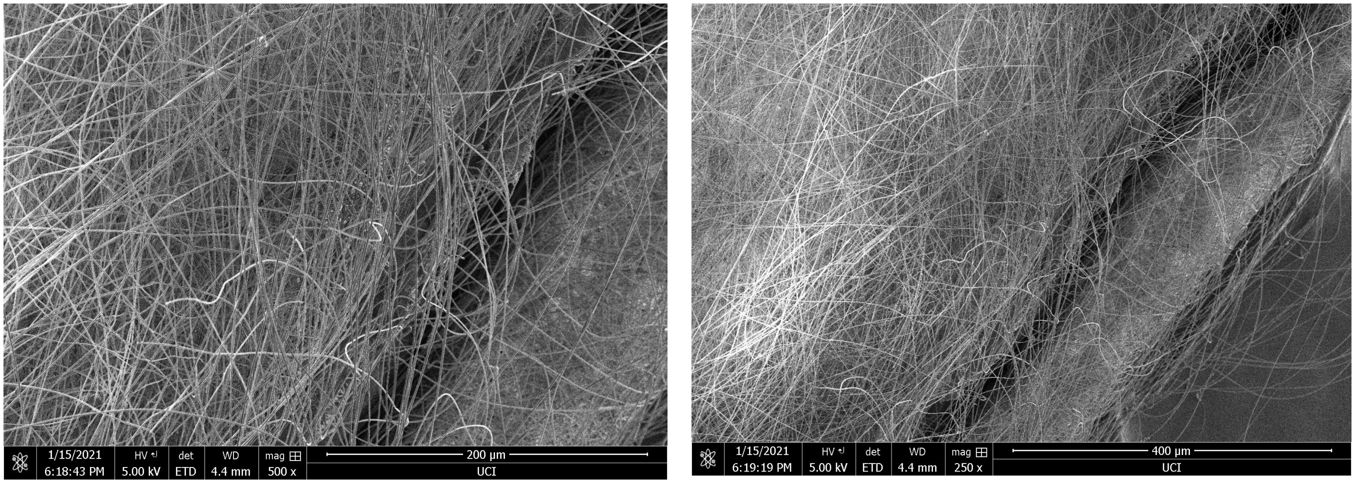
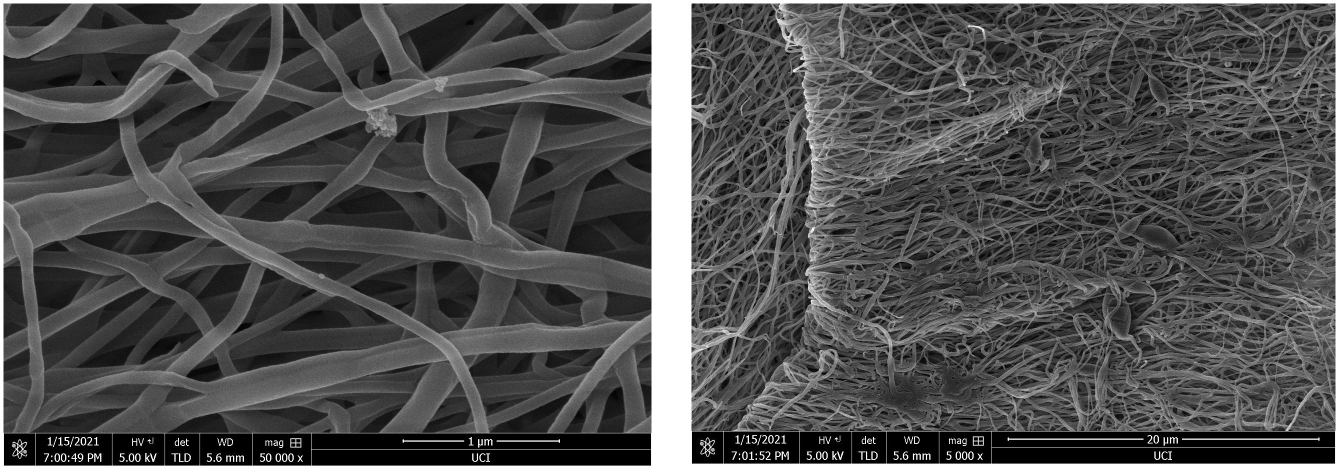
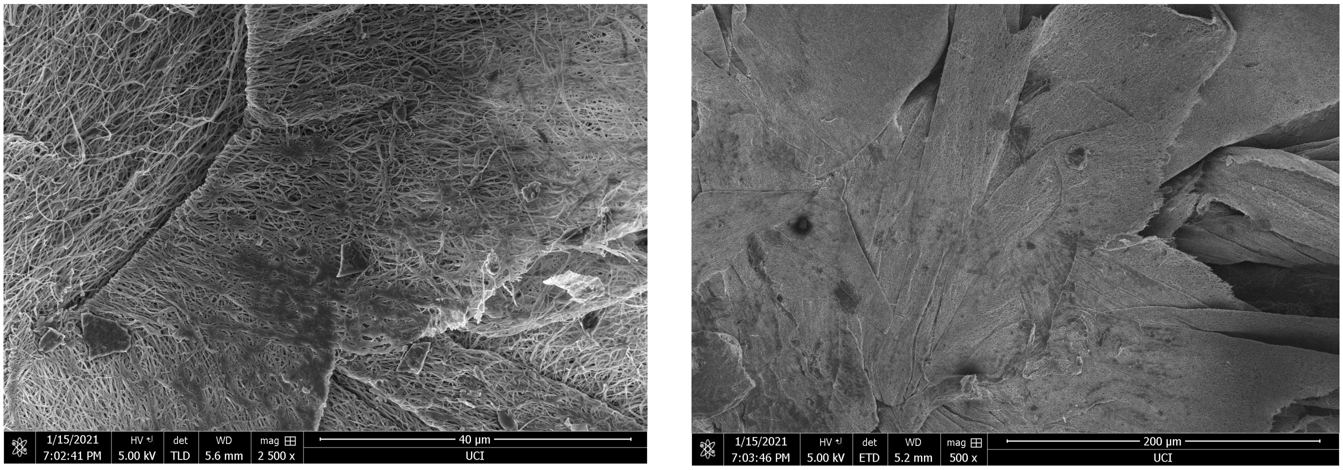


Figure 2. Shown below are SEM images of air spun PVA. The order from (a) through (d) scales down in magnification. In (d), the overall surface texture seems smooth with random splices but referencing (c) and (b) the fibers are shown to be densely packed in a woven pattern. Looking at (a) the fiber construction varies in diameters, are homogeneously smooth with pockets of impurities, and there is no general direction for the fiber placement.



a) 1 µm, WD 5.6 mm at 50,000x

b) 20 µm, WD 5.6 mm at 5,000x



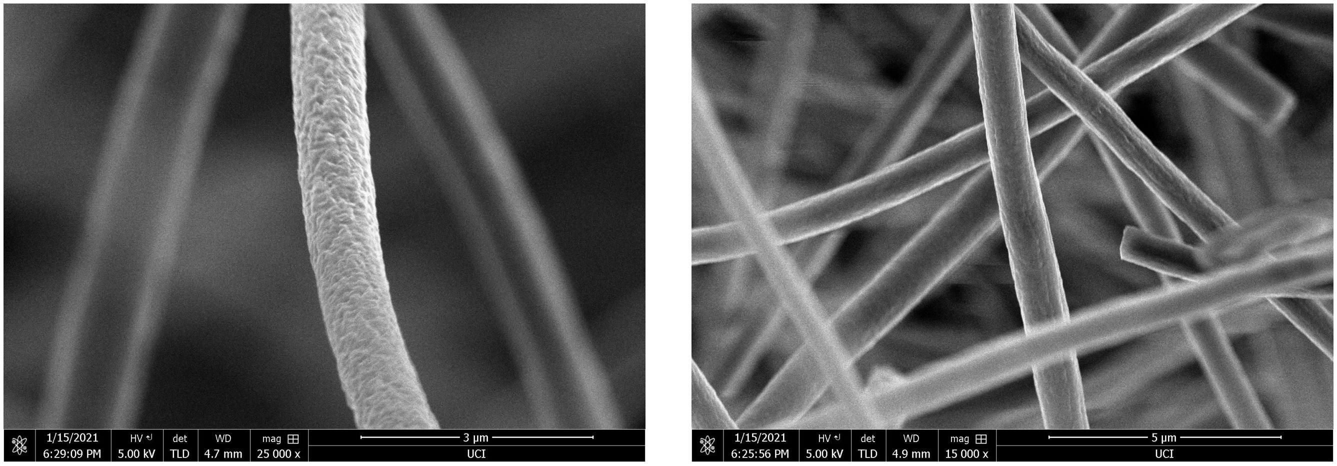
c) 40 µm, WD 5.6 mm at 2,500x

d) 200 µm, WD 5.2 mm at 500x

Figure 3. Shown below are the oxidized PAN SEM images from being in compressed air at 250℃ for 4 hours. The order from (a) through (d) scales down in magnification. The fibers have become more angled in their direction as seen in (c). Both (a) and (b) show that the fibers are still textured and each diameter is uniform among all fibers.

a) 3 µm, WD 4.7 mm at 25,000x

b) 5 µm, WD 4.9 mm at 15,000x



c) 40 µm, WD 4.9 mm at 5,000x

d) 100 µm, WD 4.5 mm at 1,000x

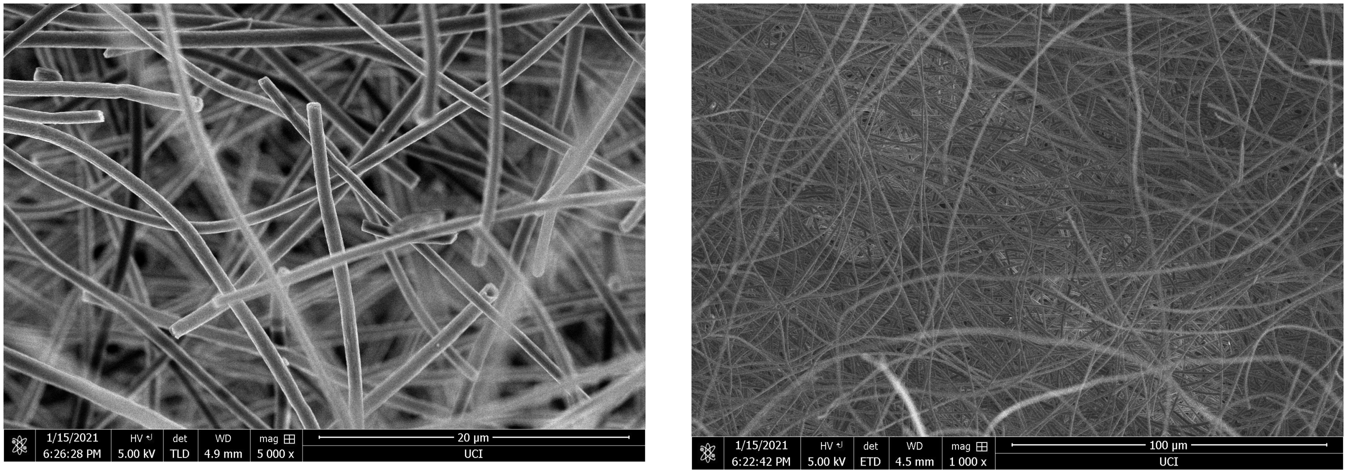
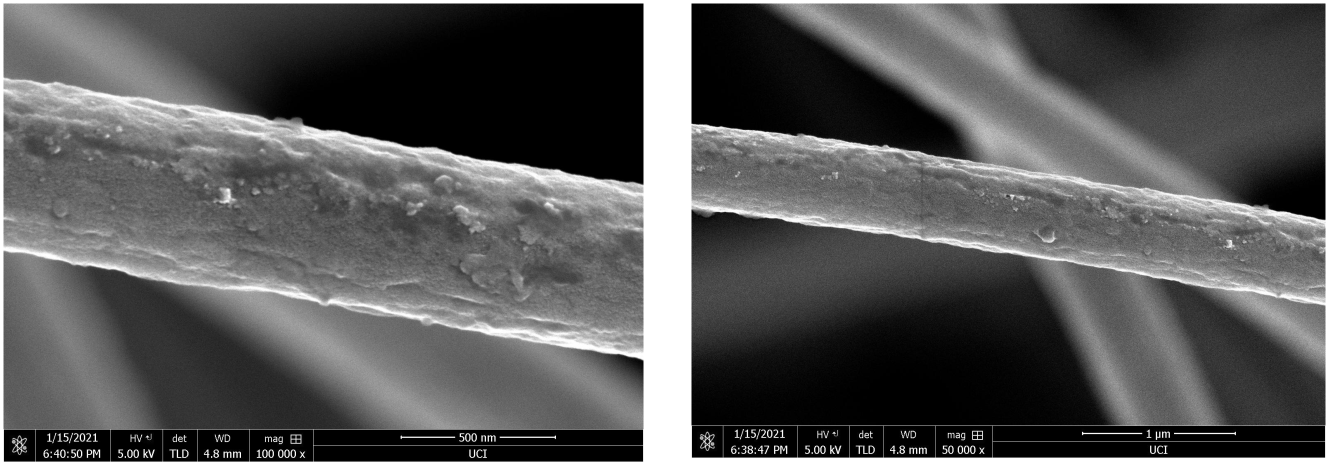
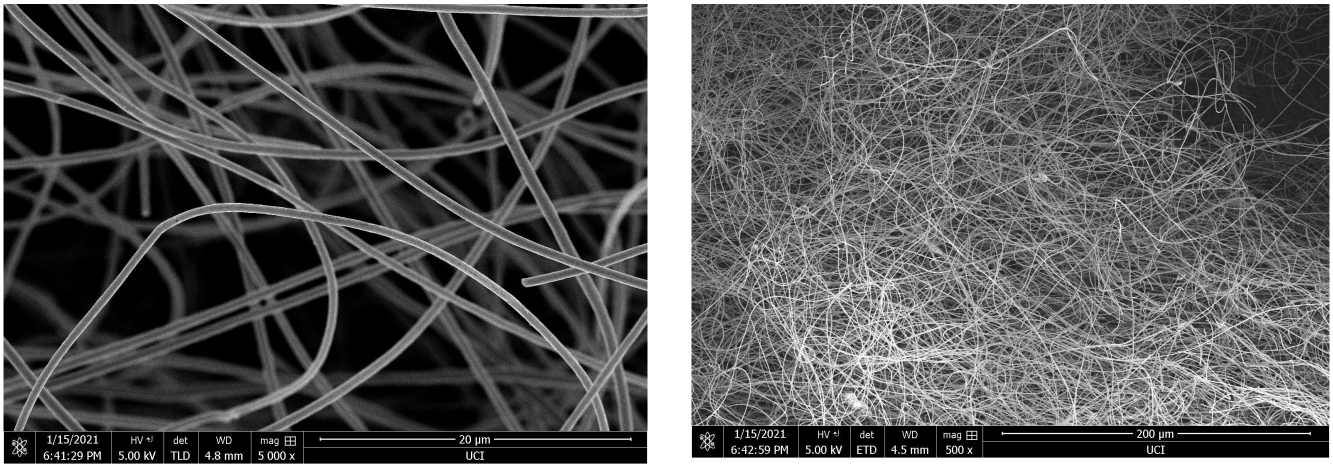


Figure 4. Shown below are the SEM images for the PAN in H2N2 gas at 1000℃ for 1 hour. The order from (a) through (d) scales down in magnification. It can be seen in image (c) that the direction and length of the fibers have become more varied by stacking on one another. Both (a) and (b) show that the texture of the fibers is still present yet have become bumpier instead of rigid as seen in Figures 1 and 3.



a) 500 nm, WD 4.8 mm at 100,000x

b) 1 µm, WD 4.8 mm at 50,000

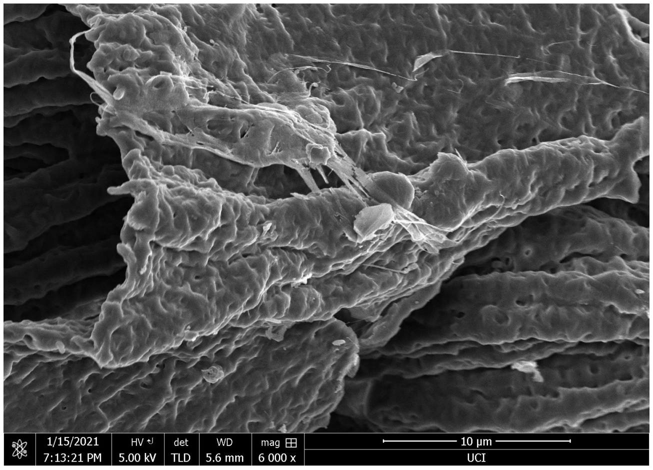


c) 20 µm, WD 4.8 mm at 5,000x

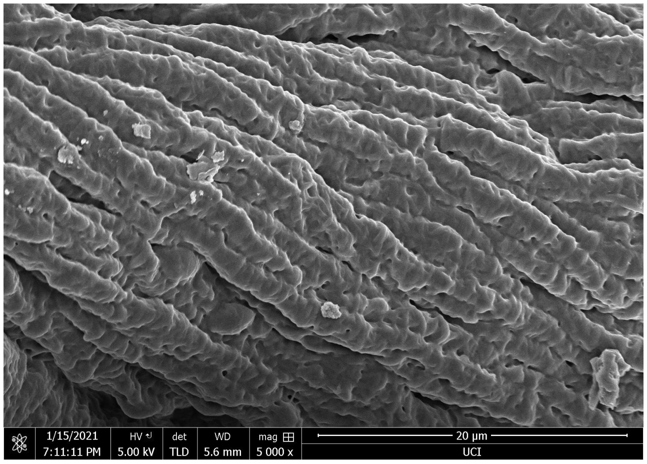
d) 200 µm, WD 4.5 mm at 500x

Figure 5. Shown below are the SEM images of oxidized PVA in compressed air at 215℃ for 2 hours. The order from (a) through (d) scales down in magnification. All images presented show the fibers in PVA have combined to form a densely packed mass of all interwound fibers. In (a) and (b) the impurities can still be seen as lighter dots. Also, in (a) the individual fibers diameter is hard to calculate and is better represented as an average bundled diameter of < 10 µm.

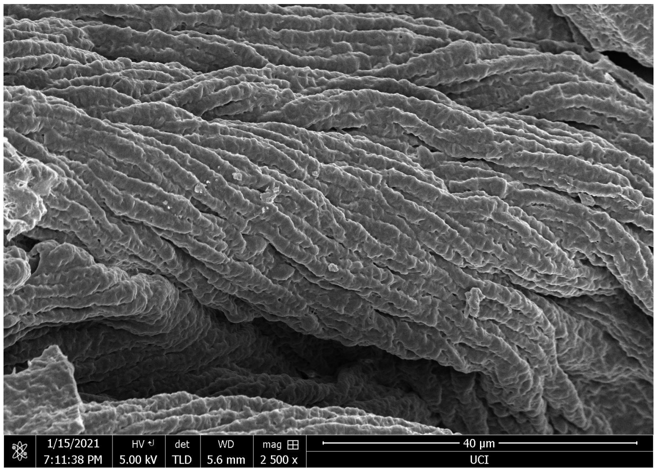
a) 10 µm, WD 5.6 mm at 6,000x



b) 20 µm, WD 5.6 mm at 5,000x



c) 40 µm, WD 5.6 mm 2,500x



d) 200 µm, WD 5.1 mm at 500x

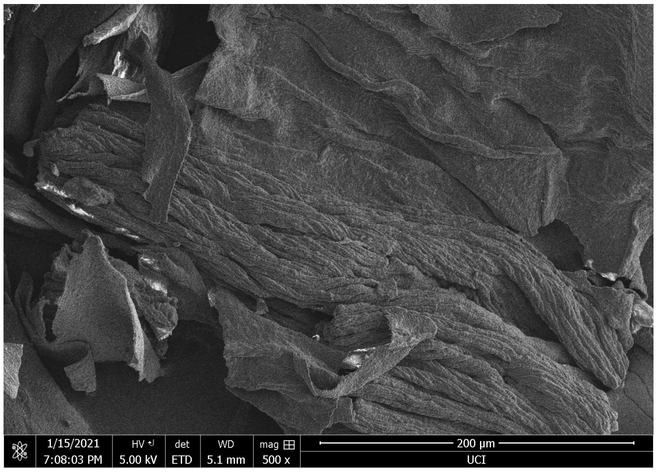
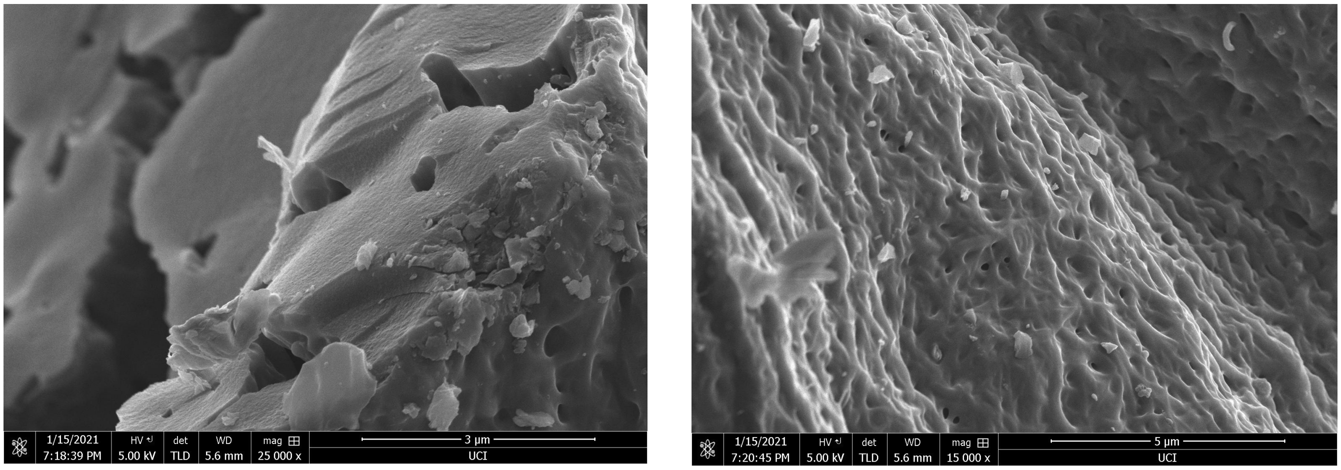


Figure 6. Shown below are the SEM images of the PVA in H2N2 gas at 800℃ for 1 hour. The order from (a) through (d) scales down in magnification. The entire surface shown in (d) has become extremely rough and layered and can be applied individually to the fibers shown in (c) and (a). Similar to Figure 5, the diameter of the fibers cannot be individually determined and will be estimated as a bundled average of > 20 µm reaching closer to 30 µm based on (c). In (a) and (b) the fibers resemble a matrix formation keeping the impurities on the surface of each fiber.

a) 3 µm, WD 5.6 mm 25,000x

b) 5 µm, WD 5.6 mm at 15,000x



c) 20 µm, WD 5.6 mm at 5,000x

d) 400 µm, WD 5.2 at 250x