Preparation of Electrospun Piezoelectric Polyvinylidene Fluoride Nanofibers

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A. ***Abstract*—This work focuses on electrospinning nanofibers for use as an alternative solution to cochlear implants to address a loss of hearing. The required diameter for self-poled piezoelectric nanofibers is 100 nm. Experiments used solutions of Polyvinylidene Fluoride (PVDF) dissolved in combinations of dimethylformamide, acetone, and a light-emitting polymer F8BT. Average fiber diameters were larger than desired. Two notable solutions yielded average diameters of 180 nm to 200 nm. High resolution scanning electron microscopy was used to characterize the fiber's diameter. Further work will have to be done to modify the electrospinning parameters to obtain the proper diameter for this application.**

Index Terms— Electrospinning, Nanofiber, PVDF, Self-poled

INTRODUCTION

Hearing loss is a significant problem that is most commonly caused by chronic and sustained exposure to high sound levels, birth defects, and/or disease. At present, hearing aids and cochlear implants are two well-developed solutions for hearing loss. Hearing aids are a valuable solution that augments the normal sense of hearing for their user. Hearing aids are based on the principle of amplification. A microphone is used to record sounds as electrical signals, which are then processed within the hearing aid. After the processing, a speaker converts the electrical signals into amplified sound waves that are directed into the user's ear. This solution is applicable when patients have mild to moderate hearing loss. This method does require that the structures of the inner ear and cochlea can still perform their normal functions despite being impaired. This impairment commonly manifests as damaged or dead hair cells within the cochlea. There must be a considerable number of surviving hair cells spread along the cochlea to allow hearing aids to compensate for some lacking hair cells. Those with severe or total hearing loss may pursue cochlear implants to provide a semblance of our natural hearing sense. These implants require electrodes to be surgically implanted within the patient's ear to provide direct stimulation to the auditory nerves. These electrodes effectively replace the cochlea and the hair cells that are used to transduce sound and convey the information to the brain. Instead the electrodes directly stimulate auditory neurons and provide a different sense of hearing. Cochlear implants also need to have a microphone for receiving sounds and a larger speech processing unit that will control the stimuli provided by the electrodes. The main complaint against cochlear implants that we wish to address is the invasive nature of the implanting process. The nanofiber based solution that my research group is working on aims to provide a minimally invasive alternative to the cochlear implant. The fibers produced will be used as replacements for the inner hair cells of the cochlea. This means our solution will be applicable when the hair cells are dead or missing but will require the rest of the inner ear to be functional.

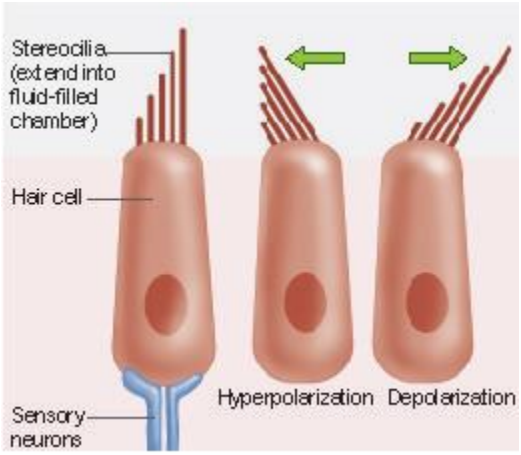

Figure 1: An image of an inner hair cell that may be replaced by the nanofiber.

Our approach will utilize piezoelectric Polyvinylidene Fluoride (PVDF) nanofibers. The nanofibers will deform due to sound wave stimuli, and transduce a current to auditory neurons. These nanofibers will replace natural inner hair cells. The stereocilia are fibers that resemble single strands of hair aligned in rows and stacked on the top of a hair cell. An image is provided in Figure 1. The stereocilia are an important part of the hair cells because their motion in the fluid of the inner ear is vital to how we naturally perceive sound. The stereocilia transduce an acoustic input into an electrical output. When the stereocilia bend they open ion channels into the hair cell which allow potassium and calcium ions into the cell body. This flow of ions is what mediates the hair cells' interaction with the auditory neuron. The neurons then communicate with the brain and provide the auditory information. It should be noted that frequency for sounds is inherently encoded by the varying lengths of the stereocilia that exist within the cochlea.

Our approach replaces the whole hair cell with a fiber or group of fibers that are piezoelectric. Piezoelectricity is a property of materials that relates to how mechanical deformations lead to the generation of an electric charge separation. The reverse is also true and is deemed the reverse piezoelectric effect. We expect to use this property to convert the movements of the fiber into an electric current to stimulate the auditory neuron.

II. Background

PVDF normally exists in the alpha phase which is not piezoelectric. In order to create fibers that are piezoelectric, the fibers must be grown or transformed into the beta phase. Electrospinning will convert PVDF stored as a powder into a fiber. The fibers may also become self-poled by the electrospinning process. Self-poled PVDF will be piezoelectric. This work is concerned with specifically conventional electrospinning. Electrospinning, as a fiber or mat fabrication technique, has been described in various ways in recent literature. Bhardwaj and Kundu [1] provide a review of recent work with electrospinning and outline the significance of electrospinning parameters. Electrospinning creates micro or nanometer scale solid fibers from a liquid solution. For many relevant applications the solution is made from a polymer dissolved in a solvent. The end goal is to obtain a fiber of the polymer without retaining the solvent. This process is accomplished by providing a solution in a syringe and ejecting the solution from a needle while simultaneously applying a large voltage to the needle.

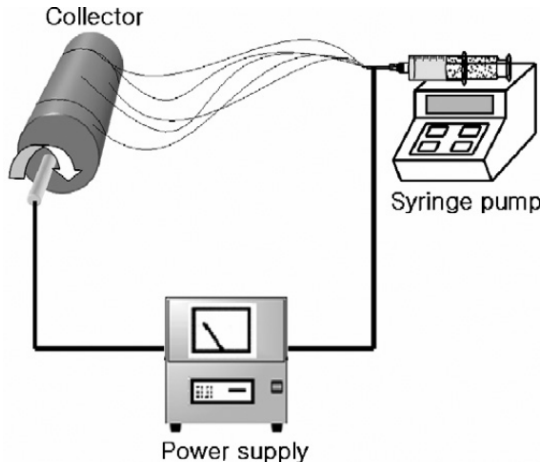

Figure 2a: Basic schematic diagram of electrospinning..

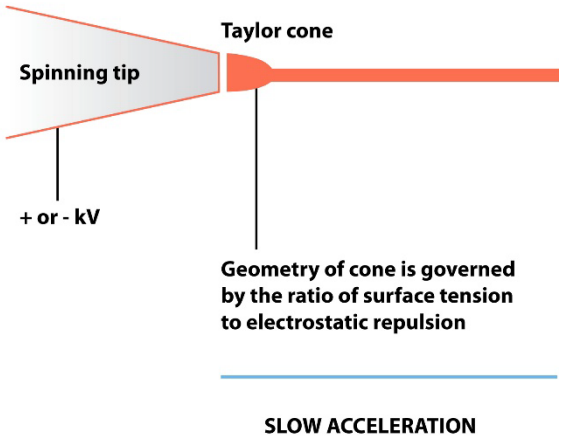

Figure 2b: Illustration of Taylor cone at the tip of a needle

A collector surface is used to obtain the fibers after the solution is subjected to a high voltage generally of the order of 10 kilovolts. Figure 2a displays a schematic of the system. The choice of collector shape and whether or not it rotates are parameters that affect the morphology of the electrospun fibers. For applications where small diameter size for fibers is desirable, a rotating cylinder is often employed to allow for some additional stretching. Rotating collectors may also produce aligned fibers rather than randomly deposited fibers. The key feature of electrospinning is the Taylor cone. If we imagine a drop of solution at the tip of a needle, the liquid will be pulled in the direction of the collector and a small jet of liquid will be constantly pulled from the solution. The initiation of this jet is dependent on the Taylor cone, which is depicted in Figure 2b. The Taylor cone itself is formed by interactions between the electrostatic forces acting on the solution and the surface tension of the solution. Charges on the liquid's surface repel each other and act against the surface tension of the solution. When a large enough voltage is applied, the electrostatic repulsions are strong enough to cause the Taylor cone to form and a charged jet of the polymer to be discharged. This jet directs the solution in the direction of a lower voltage source. Generally a grounded collector is used in tandem with a high voltage supply. While the solution is charged and moving towards the collector the solvent evaporates quickly depositing the solid polymer. The motion of induced dipoles in the non-homogeneous electric field may also affect the deposition. The electrospinning process has various parameters that may be altered. These are placed in broader categories. Namely, solution, processing and ambient parameters.

The present application will require fibers that range in diameter from 50-100 nanometers. This size requirement is based on the need for self-poled fibers. The phase of the PVDF will also be converted to the beta phase from the alpha phase. These self-poled fibers will be piezoelectric. The size requirement is a major factor in determining the parameters for the spinning process. One challenge that will complicate

this work is the need to include fluorophores into the polymer solutions. This will aid in a demonstration where the fibers are implanted within test mice. The fluorophore will acts as a method to track the location of these fibers to ensure their successful delivery into the inner ear. The progress of the fibers inside a mouse's inner ear will be checked inside an in vivo molecular imager made by Bruker. The fluorophore is excited by a specific wavelength and will re-emit light when stimulated by that wavelength.

III. Experimental setup

IV. 3 Experimental Details:

For this project, PVDF with a molecular weight of 534,000 was purchased from Sigma-Aldrich. The solvents used include N, N- dimethylformamide (DMF, D4551), acetone (534064) and chloroform (C2432) from Sigma-Aldrich as well as reagent grade toluene from Fisher Science Education (S25611).The fluorophores tested were F8BT and MDMO-PPV both purchased from Sigma-Aldrich. The diameter of PVDF fibers was measured in a Jeol 7500F high resolution scanning electron microscope (HRSEM). The microtome used was a Leica RM2125 rotary microtome.

The preparation of nanofibers was accomplished with conventional electrospinning. Our electrospinning setup was slightly modified from the aforementioned system by the addition of a stepper motor which moved the syringe pump during the spinning process. The syringe pump had a horizontal translational motion that spread the fibers across a wider area of the collection cylinder. The rotating cylinder collector was always covered by a sheet of aluminum foil to act as a substrate for the deposited fibers.

A few different solutions were prepared in order to test if they could be electrospun and to determine the associated average diameter for the fibers. The solutions that were most thoroughly examined were solutions made from 18 weight percent (wt. %) PVDF dissolved in DMF and Acetone in a 3:1 volume to volume ratio with the inclusion of F8BT as well as, 16 wt. % PVDF dissolved in DMF. When preparing the solutions, PVDF was always added to a vial first, then DMF was added followed by the acetone if it was needed. This procedure was chosen to help limit the evaporation of acetone. In order to incorporate the fluorophore into the polymer solution it was dissolved in one of the solvents. This was accomplished by dissolving a small amount of F8BT in chloroform then putting that solution in a mixture with acetone.

Both solutions were placed on a hot plate around 50°C and set to stir before being used to electrospin. The PVDF and DMF samples stirred for an hour to allow for the PVDF to fully dissolve and a homogenous solution to be obtained. The solutions with acetone were left stirring overnight before being used for electrospinning.

Samples of 18 wt. % PVDF dissolved in DMF and acetone with F8BT were electrospun with a needle-to-collector distance of 10 centimeters, at 13 kilovolts, with a solution flow rate of 0.5 milliliters per hour. Samples of 16 wt. % PVDF dissolved in DMF were spun at 15 centimeters, at 15 kilovolts, with a solution flow rate of 0.70 milliliters per hour.

The diameter of electrospun samples was investigated through the use of scanning electron microscopy (SEM). Only samples that seemed to form a stable or periodic jet were investigated by SEM. Samples that electrosprayed or drew droplets from the solution instead of a jet were not pursued. The samples were characterized either as a mat deposited on aluminum foil or as fibers drop cast onto a stainless steel puck.

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V. Experimental Results

Figures 3 and 4 are SEM images for the 18 wt. % solution with the fluorophore and the 16 wt. % PVDF solution respectively. Several images of both samples were captured in order to measure the diameter of fibers present. Data for the fiber diameter measurements from each sample are provided in Figure 5.

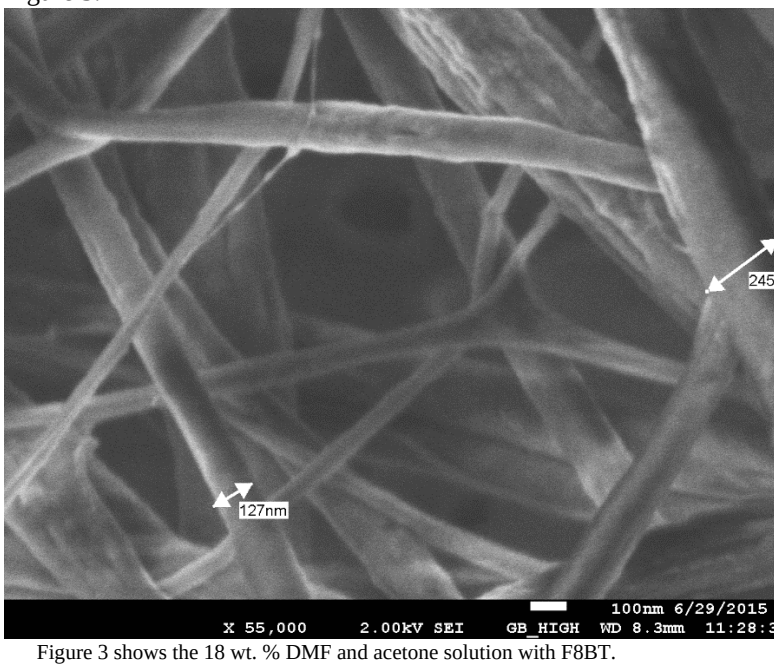

Figure 3 shows the 18 wt. % DMF and acetone solution with F8BT.

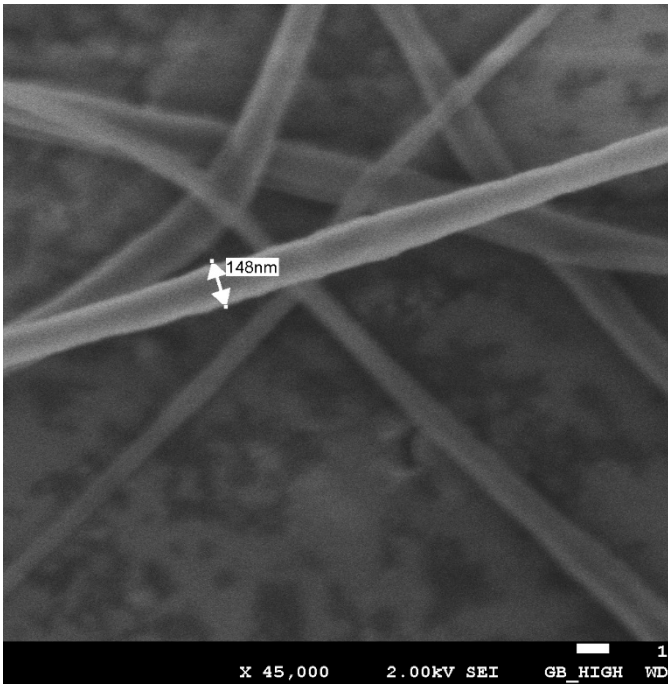

Figure 4 depicts the 16 wt. % PVDF in DMF.

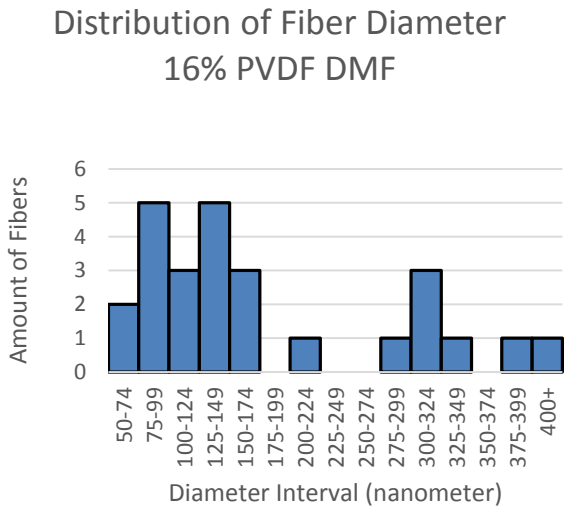

Figure 5a: is a histogram of the frequency of different diameters for the PVDF dissolved in only DMF.

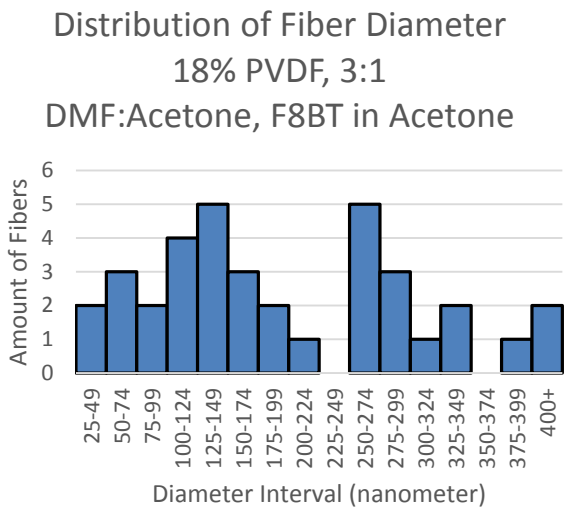

Figure 5b is a histogram of the frequency of different diameters for fibers with F8BT.

Average diameters and standard deviations measured were 200 nm for the diameter and 110 nm for the standard deviation of the solution with the fluorophore. The solution of 16 wt. % PVDF and DMF had an average diameter of 180 nm, and a standard deviation of 118 nm. The previous values were obtained through measurements of fibers present in SEM images. Three pictures of different locations were taken for each solution. We expect that the electrospinning process should generate a log-normal distribution in terms of the diameters of the fibers.

VI. Discussion and Conclusion

The wide distribution of sizes for the nanofibers is an issue that will reduce the yield of the electrospinning process. One factor encouraging such a large distribution is the inconsistent nature of the polymer jets being formed. The jet should form from a drop of the solution and stay consistent in the direction it points, the length of the jet and flow rate of the jet. However, while spinning these solutions the jet would change in periodic fashions. For the fluorophore sample this would include behavior where the jet appears and then grows larger as more of the solution is pulled in an instant and then the jet shrinks back down to its original size. One problem unique to the fluorophore enhanced samples was the requirement of adding trace amounts of chloroform to dissolve the fluorophore. The poor mixing between chloroform, acetone and DMF may have led to the aforementioned problem with the consistency of electrospinning. The PVDF and DMF sample had a different problem. For those samples the jet would change direction and length constantly during the process but would seem to be spinning a steady amount of the solution at any time.

The average diameters presented were too high for our desired application but there are some options to shrink the diameter in future studies. One choice is to increase the rotational speed of the collector. At present the collector rotated at about 140 rotations per minute. Other papers that

looked into similar solutions used 550 rotations per minute for their electrospinning. It should be noted that the size of the collector is also important when it comes to considering the rotational speed needed. Modifying the applied voltage, needle-to-collector distance and solvent choice are also options that may shrink the diameter.

ACKNOWLEDGMENT

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