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Different Parameters Affect the
Properties of Polyvinylidene Nanofibers

Abstract

Many cases of hearing loss arise from damage that occurs to hair cells located inside of the cochlea. The use of the biocompatible and piezoelectric material polyvinylidene fluoride (PVDF) is being studied as a possible substitute for the damaged hair cells. More specifically, PVDF in the beta phase is of main concern because this is the phase in which it shows signs of being piezoelectric. A maximum amount of piezoelectric response is desired, therefore the process that makes PVDF piezoelectric must be optimized. The aforementioned process that PVDF must go through is called poling, where the created sample is heated and exposed to an electric field. In doing so, the individual dipole moments of the molecule will be aligned to face similar directions, which makes the piezoelectric characteristics emerge. The point of heightened induced piezoelectricity in our poling setup is found by varying the voltages at which the sample is poled at. In doing so, the optimal poling setup for inducing piezoelectricity in PVDF is found. In this study, Piezoresponse force microscopy was used to measure levels of piezoelectricity in the samples and their physical properties. These results have made it possible to achieve higher piezoelectric levels in PVDF.

Introduction

        Various reasons that could lead to the development of hearing loss in individuals includes damage done to the ears, the aging process, and illnesses (1). One cause for why hearing loss occurs can be explained after taking into consideration the structure of the inner ear. Inside of the inner ear exists a snail shaped structure referred to as the cochlea. This structure is filled with both electrolyte rich fluids, endolymph and perilymph, which vibrate the hair cells located inside of the organ of the corti after experiencing the mechanical force that is induced by sound. On each hair cell, there exists a small patch of hair-like projections called stereocilia. When bent, the stereocilia cause the opening of cation channels, where potassium and calcium ions from the endolymph enter the hair cell causing it to depolarize. After stimulation of these cells occurs, electrical signals are sent along the auditory nerve to the brain which are interpreted as messages that humans can recognize (2). Often, because of some sort of trauma such as a very loud noise, the stereocilia become bent or even broken. This in turn causes the hair cells to become critically damaged causing them to either die or become useless, leading to hearing loss (3).

        One method of correcting hearing loss is cochlear implant surgery. In cochlear implant surgery, the cochlear implant used involves an external portion and an internal portion that is surgically placed underneath the ear skin. While hearing aids work to amplify sounds, cochlear implants directly stimulate the area that is responsible for converting electrical signals from the hair cells to distinguishable sounds (the auditory nerve). In picking up sound, the transmitter of the cochlear implant converts the signals received to electrical impulses, which are sent to its electrode array. The electrode array then sends these impulses to multiple areas of the auditory nerve, allowing for sound to be recognized by the individual (4). The surgery, while effective in many cases, is invasive to the individual's inner ear. A method used to avoid such a surgery can be developed through the use of piezoelectric materials. Our lab has taken the approach of using a biocompatible and piezoelectric polymer called polyvinylidene fluoride (PVDF).

PVDF exhibits its piezoelectric characteristics when it is present in the beta phase. Not only is PVDF (**β**) a piezoelectric material, but it is also highly non-reactive and therefore biocompatible (5). These qualities make PVDF a reasonable candidate for the development of piezoelectric nanofibers that could potentially work to replace the function of damaged hair cells. For this reason, PVDF is selected as the primary study material in our lab.

Background

The alternative to the cochlear implant surgery would be to use a biocompatible, piezoelectric material as a replacement mechanism for the damaged hair cells. Piezoelectric materials are materials that when exposed to a mechanical stress, generate an electrical charge. To further understand this phenomenon, the molecular scale of a material must be considered. When speaking on the molecular scale, as a result of a non-centro symmetric crystalline structure, an electric polarity will exist. This also means that the unit cell is itself an electric dipole. The application of mechanical stress further increases the displacement of the central atom therefore creating a stronger polarization in the molecule (6). Fundamentally, this is how the piezoelectric effect comes to be. The dipoles of a non-piezoelectric material are initially facing random directions, so if a mechanical stress is applied to the material, the rotation of the randomly oriented dipoles will not greatly affect the net polarization of the molecule. When all of the dipoles are facing the same direction, however, the net polarization of the molecule is substantially affected which would lead to a notable piezoelectric effect. A material can be made to be piezoelectric through the use of poling in which the dipoles of the material are arranged towards the direction of an applied electric field. When the electric field is removed, many of the dipoles will remain oriented towards the same direction. In the poling process, the addition of heat is involved because, for certain temperatures, the piezoelectricity exhibited is higher than it would be without the addition of heat. This is because the added heat increases the alignment of the dipoles (7). At the end of the poling process, the sample is cooled while the electric field is maintained in order to lock in the polarization domains (8). If the material is heated to a higher temperature than the Curie temperature, however, then the material will no longer exhibit piezoelectricity. That is, when the Curie temperature is reached, the system stops being ferroelectric and becomes paraelectric, meaning that the material cannot retain spontaneous polarization properties (9, 10).

Again, in order for its piezoelectric properties to be exhibited, PVDF needs to go through poling. The solution that is used to prepare PVDF also includes the addition of a fluorophore (Rhodamine B), which is a molecule that will emit fluorescent light when exposed to light excitation with a wavelength of about 500 nm (11,12). The use of a fluorophore is the method that will help verify whether or not the PVDF nanofibers actually make it into the inner ear. In order to maximize the characteristics that would make the most effective PVDF nanofibers, the uniformity of the nanofibers, the amount of Rhodamine B added, and the induction of piezoelectricity through the specific poling procedure used is being taken into consideration. The poling procedure used involves a set up that can both heat and apply a voltage to the sample that will lead to measurable piezoelectric characteristics. The research conducted will explore the necessary voltage required to pole a sample, and how the magnitude of voltage applied will affect the results. After each sample is poled, they will be analyzed through the use of Piezoresponse force microscopy (PFM). Using the data acquired from these techniques, the conditions from our poling procedure that would most highly affect the piezoelectric properties in PVDF can be made apparent.

Experimental

4.1 Materials

Acetone (serial number 534064), dimethylformamide (DMF, serial number D4551), polyvinylidene fluoride (PVDF), and rhodamine B purchased from Sigma-Aldrich were chemicals that were used in the making of the solution used. For the poling setup, two copper electrodes, two 3mm thick slabs of polydimethylsiloxane (PDMS), a hot plate, and a high voltage DC supply (Spellman, serial number 0007286) were used. Collection of the created films from the PDMS was done with plastic outlines that were rimmed with double sided tape. The films were then transferred to a copper film and held in place with more double sided tape. Analysis of the films was done through the use of an Asylum atomic force microscope.

4.2 Methods

A solution of 5 percent weight PVDF in acetone and DMF was made, Rhodamine B included. The solution was a 1:3 (acetone: DMF) volume ratio, and to include the fluorophore into the solution, it was added into the acetone first to achieve a concentration of 0.01 mg/mL. To create the solution, the given amounts of each material were placed into a 20 mL vile in the order of PVDF, DMF and Acetone. This particular order prevented an excess amount of acetone evaporating since it is the most volatile. The solution was heated to around 50 degrees Celsius. Thirty minutes of continuous heating and stirring was a reasonable amount of time to allow for the PVDF to dissolve, and for the mixture to become a homogenous clear liquid. More time on the heat was allowed if needed.

To perform the poling of the solutions, a hot plate was first set to preheat to 90 degrees Celsius. While it was preheating, the surfaces of PDMS were cleaned with isopropyl alcohol to help provide a clean and uniform surface for the PVDF films to form. After having the PDMS prepared, the first electrode was placed on top of the hot plate, copper side up. Following the electrode, the PDMS slab was placed. After this, an amount of PVDF solution that ranged from 500 mg to 700 mg was carefully poured onto the center of the PDMS. After having poured the liquid onto the PDMS, the other PDMS slab was quickly placed on top to prevent evaporation of the solvents. Finally, the second electrode was placed on top of the PDMS, copper side down. In total, the electrode separation distance was about 6 mm in height. A 100g weight was also placed on top of the setup to help secure it. An image of this setup can be seen by figure 1. The bottom electrode was grounded, while the top electrode received an amount of voltage ranging from 5 kV to 7 kV. At the moment that the voltage was applied, the heat was raised to 180 degrees Celsius for five hours. Midway through, the temperature was measured using a Seek Thermal compactXR thermal imager. The system was allowed to cool for one hour during which the voltage was not turned off. When the sixth hour was complete, the voltage was switched off.

Figure 1. Poling setup used to pole 5% PVDF solution

Once the procedure was complete, the collection of the PVDF films could be done. The frames that were used to collect the PVDF films were laser cut plastic frames, which can be seen in figure 2. These frames were covered with double sided tape, which were cut so as to leave the middles of them hollow. In doing so, a stamp of sorts was created which made it possible to be pressed onto the PDMS surface and carefully collect the film that was formed. The desired result would have been to collect film that was flat which would have made it easier to cut with an excimer laser. This process was repeated until most of the film formed was collected onto the frames. After being collected on the frames, a piece of double sided tape was placed onto a piece of copper film, where the PVDF films were transferred to (figure 2).

Figure 2. Plastic frames used to collect PVDF films from the PDMS and the copper substrate used to collect the film from the frames.

Results

During the poling process, because of heat loss through conduction, the heat that actually reached the PVDF solution only increased its temperature to around 40 degrees Celsius for each sample as opposed to the set 180 degrees Celsius. Images of the temperature measurement for each sample can be seen in figures 3-5.
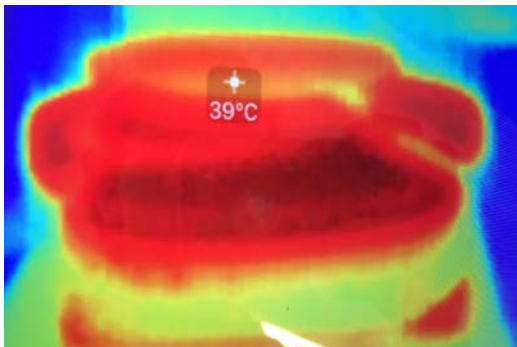

Figure 3. Thermal image of hot plate, electrode and PDMS setup, with 5 kV of applied voltage on PVDF sample.
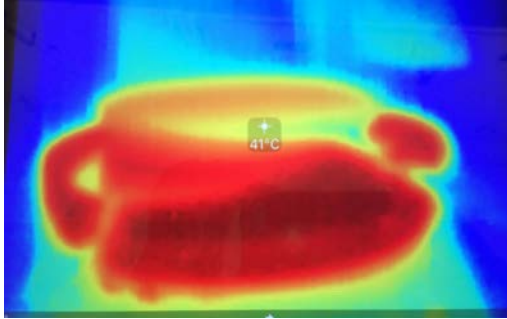
Figure 4. Thermal image of hot plate, electrode and PDMS setup, with 6 kV of applied voltage on PVDF sample.
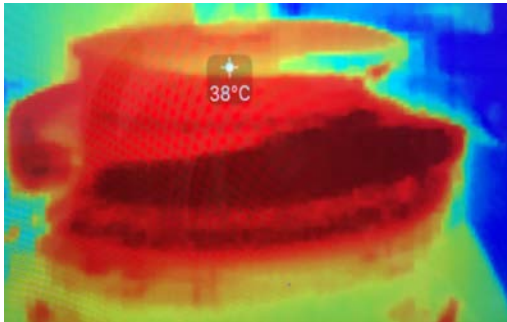

Figure 5. Thermal image of hot plate, electrode and PDMS setup, with 7 kV of applied voltage on PVDF sample.

The surface of each film created and the piezoelectric response was analyzed through the use of Piezoresponse force microscopy. The amplitude maps generated in PFM describe the piezoelectric responses of the samples. The amplitude maps of the highest response for each sample can be seen in figures 6-8, while figure 9 shows the piezoelectric response of the copper film on which the samples were placed on. All samples were driven at a voltage of 3V during PFM.
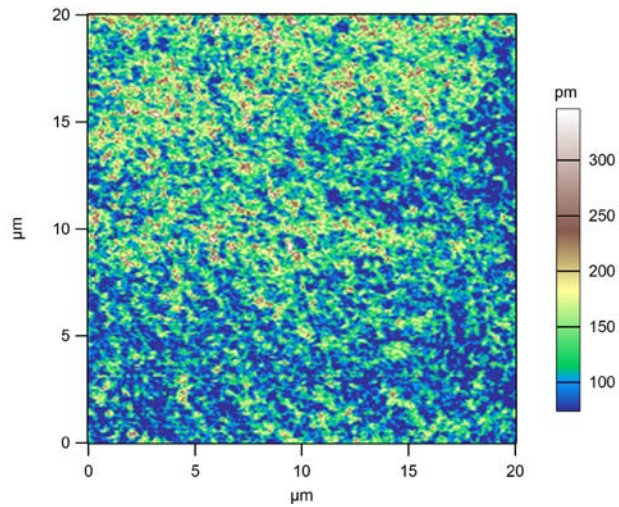
Figure 6. Amplitude map of PVDF poled at 5 kV. During tuning, frequency was 314.945 kHz at a peak of 629.425 μV.

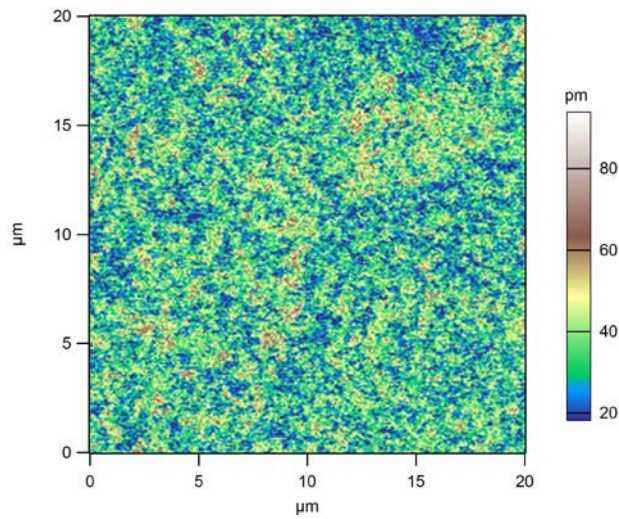
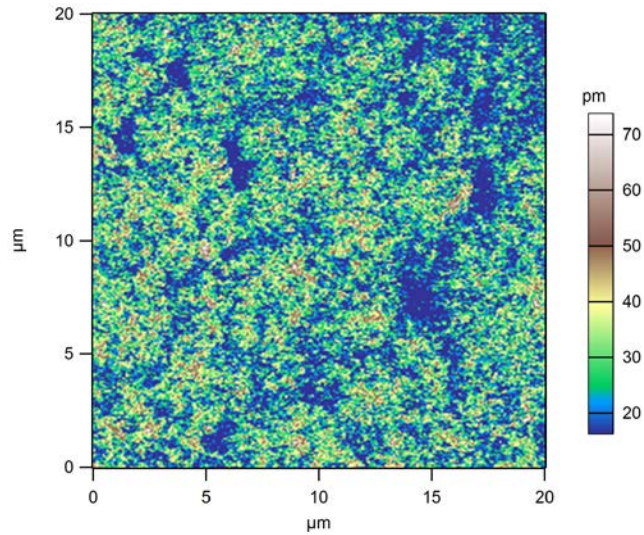Figure 7. Amplitude map of PVDF poled at 6 kV. During tuning, frequency was 296.118 kHz at a peak of 641.346 μV.

Figure 8. Amplitude map of PVDF poled at 7 kV. During tuning, frequency was 289.716 kHz at a peak amplitude of 660.419 µV.
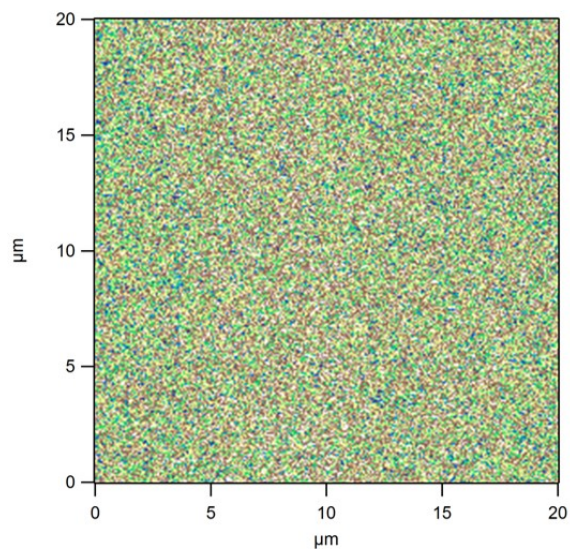

Figure 9. Amplitude map of copper film that was used to hold the samples. During tuning, frequency was 328.757 kHz with a peak amplitude of 1.455 mV.

The topography of the samples can be seen in figures 9-11 for each poling voltage, where they are plotted with their respective amplitude maps overlaid on top.
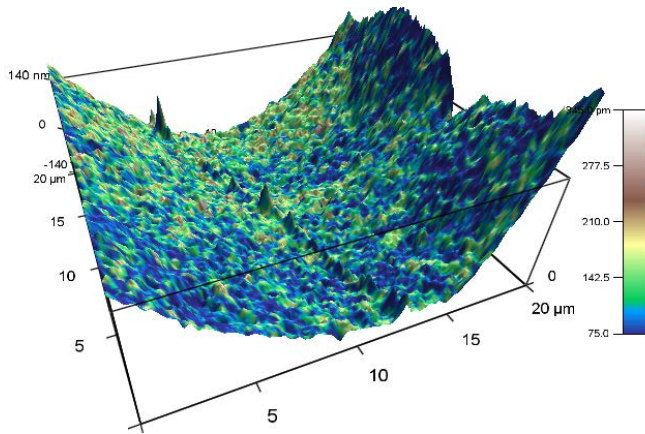
Figure 10. 5 kV poled sample. Amplitude overlaid on topography.
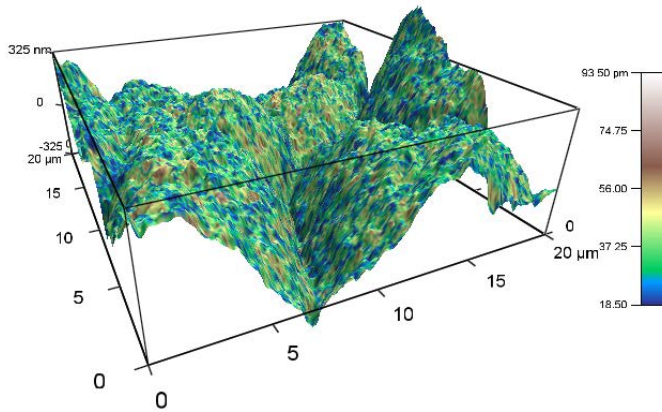

Figure 11. 6 kV poled sample. Amplitude overlaid on topography.
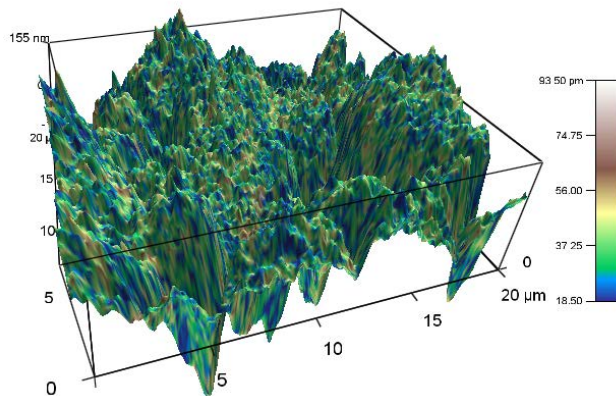

Figure 12. 7 kV poled sample. Amplitude overlaid on topography.

The piezoelectric coefficient (d_{33}) was estimated using the equation given by Asylum research [13].

$$A = d_{33}QV \tag{1}$$

Where A is equal to the amplitude reached by the sample, Q is the quality factor of the sample, and V is the drive voltage used during Piezoresponse force microscopy. The quality factor was estimated through the use of a commercially poled PVDF film (Measurement Specialties Inc., 1-1004347-0). The commercial film underwent PFM analysis at several drive frequencies in order to collect multiple Q values. The applied voltage during PFM (3V) and the d_{33} (33 pm/V) of the film were known, while the amplitudes of the film were measured (using the highest values reached), leaving the quality factor to be solved for. Using the values of Q calculated from the film, an equation relating the tuning amplitude and the quality factor was created. This was then used to estimate the quality factor for our poled PVDF films, giving us enough information to estimate the d_{33} values.

Table 1: Values for Commercial PVDF film

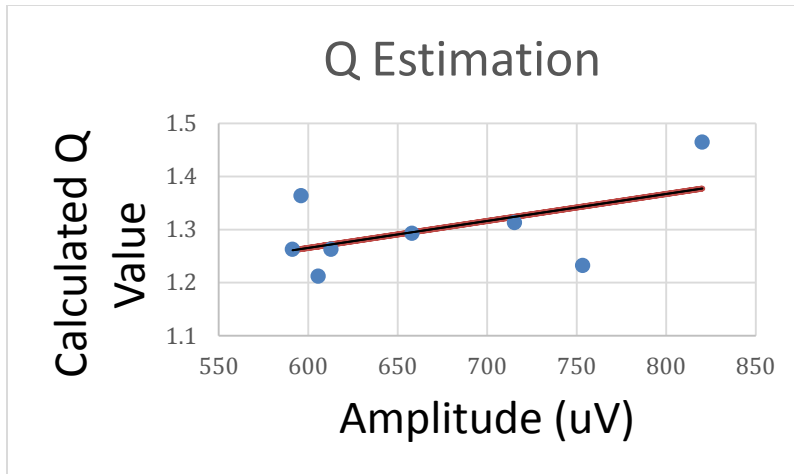| Amplitude (uV)	Amplitude Reached (pm)	Calculated Q
612.736	125	1.263
596.056	135	1.364
591.278	125	1.263
658.035	128	1.293
715.256	130	1.313
820.16	145	1.465
753.403	122	1.232
605.583	120	1.212

Figure 13. Data for Q values of commercial PVDF films collected. Line of best fit given By $Q = 0.0005A + 0.9606$ (±0.003 uV^{-1} for slope and ±0.2 for intercept).

Table 2: Our PVDF Films Estimated Q Values

Voltage Applied (V)	Amplitude (uV)	Q
5	629.425	1.280
6	641.346	1.286
7	660.419	1.296

Table 3: d_{33} for Common Amplitude Values

Voltage Applied (V)	Max Amplitude Reached (pm)	d33 (pm/V)
5	80	20.83
6	20	5.182
7	15	3.858

Table 4: d_{33} for Maximum Amplitude Values

Voltage Applied (V)	Max Amplitude Reached (pm)	d33 (pm/V)
5	250	65.09
6	80	20.73
7	70	18.00

Discussion & Conclusion

  For our project, the highest d_{33} coefficient is desired in analyzing the piezoelectric properties of any of our PVDF films generated. By solely looking at the generated results, it can be concluded that the piezoelectricity is affected negatively by the addition of higher voltages for the temperature tested. That is, at the set temperature used, the highest d_{33} value seen was at 5 kV as opposed to 6 or 7 kV. The measurements collected through Piezoresponse force microscopy can be, however, quite tricky to do. Correct placement of the sample onto the sample holder must be done so that the cantilever will be able to probe the surface, and a similar tuning to a sample with known values must be performed in order to get accurate results. One possibility for why the 6 kV and 7 kV samples did not get as high of a response as the 5 kV sample did was because the actual poling of the samples could have been flawed. A higher temperature reached by the PVDF, for instance, might have benefitted the measurable characteristics of the films created. The possibility that there is a relationship between the addition of heat and the addition of voltage when it comes to piezoelectricity is also likely. The temperature values were not varied here, so it would be very beneficial to do more research to see how the magnitudes of each affect the other with respect to piezoelectric characteristics.

  Future studies would benefit from knowing that a completely flat sample is easiest to work with when using Piezoresponse force microscopy. Also, the use of a commercially poled PVDF film with a known d_{33} is useful to more accurately calculate the d_{33} of the PVDF samples. Repetition of the experiment with thicker films would be useful, and, when concerned with solely the characterization of the films, then the collection of films by poling directly onto a non-piezoelectric material from the very beginning could be done in order to improve the process. Also, the results that would emerge from measuring the piezoelectricity in poled samples that didn't include the addition of Rhodamine b would be interesting to see.

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