Surface Bioengineering on a Triboelectric Nanogenerator (TENG) Device

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Abstract

Using biocompatible materials to develop inexpensive, self-powered devices is significant for novel clinical applications. Here we report the engineering optimization on a set of self-powering triboelectric nanogenerator (TENG) devices. These thin, film-based devices are made from a solution of alginate, a biocompatible polysaccharide derived from seaweed, and glycerol, a plasticizer which makes the films stronger and more ductile. This TENG device converts otherwise wasted mechanical energy to electricity through the triboelectric effect, which harnesses the friction energy produced from the contact electrification between two different materials. The TENG consists of two nodes on a linear motor, and produce electricity when one node contacts and then separates from the other node. Both nodes have a base of Polymethyl methacrylate, underneath a layer of aluminum (the conductive layer). Then, one node is covered with a layer of Polytetrafluoroethylene polymer, and the other, with the biopolymer film.

We optimized critical parameters such as the separation distance between the two TENG nodes, and the glycerol concentration(s) that enable the TENGs to generate the highest outputs of voltage, current, and amount of electric charge (V, I, Q). The TENG device without glycerol generated the highest voltage output, but showed unwanted brittleness, while the lowest glycerol concentration showed a small decrease in voltage but greatly increased durability. This trend suggests an optimal window for the device-fabrication parameters between the decreasing voltage output and the increasing glycerol amount. We have also identified the ideal separation distance between the two TENG nodes which generates the highest electrical outputs. Thus, an optimized biopolymer-TENG device from this systematic engineering study could self-power a wide range of medical devices.

Introduction

Renewable energy sources have emerged as an important field for innovation, especially with regards to wearable, marketable, and implantable medical devices. This is partly due to the detrimental impacts fossil fuels and disposable batteries have had upon both our environmental and physical health. As one of the most promising new forefronts in biomedical engineering, creating self-powered biomedical devices, especially those that are both biocompatible and antimicrobial, is of extreme significance. For instance, doctors often want to monitor the conditions of people with chronic illnesses. The current solution to this problem is to request that the patient use an ambulatory system. However, ambulatory systems are not a good solution when the patient needs to be monitored for any period of time longer than one or two days [1]. Ambulatory systems are usually large and somewhat bulky, often with a rolling base design that can make many daily activities difficult [2]. Wearable devices are small and discreet, providing the perfect solution for any type of long-term patient monitoring [3]. Such biocompatible and antimicrobial, wearable devices would have a broad range of applications in both clinical and healthcare-industry settings.

Triboelectric nanogenerators (TENGs) are able to convert otherwise wasted mechanical energy into electricity through the triboelectric effect and electric induction, making the use of TENGs highly applicable in device design. Essentially, TENGs harness the energy that is produced from the friction generated from the contact electrification between two different materials [3]. TENG devices could eventually eliminate the need for batteries in many smaller electronic devices due to TENGs' self-powering capabilities and low manufacturing cost [3]. Though there are several different types of TENGs, this research is concerned with the vertical contact-separate mode TENG devices. As seen in Figure 1a below, vertical contact-separate

mode TENGs are made up of two different nodes, each covered with a different dielectric film. The dielectric films are arranged to face one another. Vertical contact-separate mode TENGs generate periodic amounts of voltage, current, and electrical charge due to the constant contact-separate cycle. This periodicity is influenced by the separation distance between the two TENG nodes, as well as the speed, acceleration, and deceleration of the two nodes. When the two dielectric films contact each other, two oppositely charged surfaces are created, which is known as the triboelectric effect. As the two TENG nodes are released from contact with each other, an electrical field is generated between the two oppositely charged film surfaces, which causes a potential difference between the two electrodes [3].

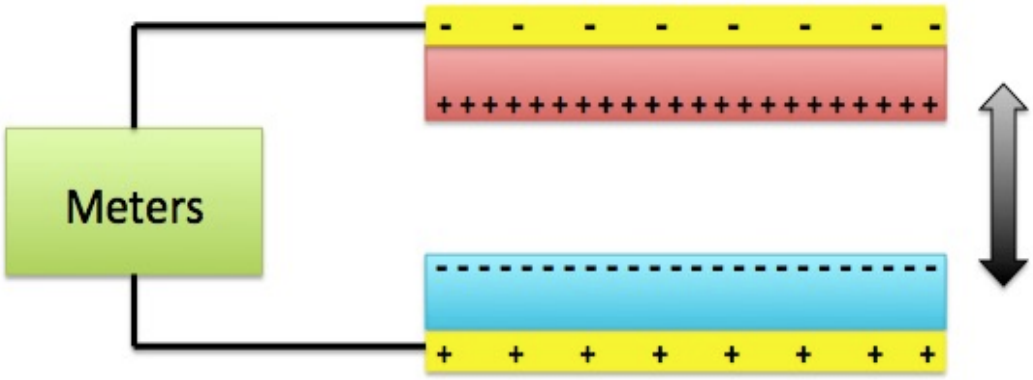

Figure 1a: The figure above shows the structure of a vertical contact-separate mode TENG device, as well as how the contact electrification occurs. The arrow shows how the two TENG nodes contact and then separate from each other.

However, until very recently, TENGs have experienced low electrical outputs in environments with a high relative humidity, which is an obvious issue for biomedical applications. Within the body, there is a considerably large relative humidity, and many common bodily functions result in some form of perspiration, which also generates a higher than normal

amount of relative humidity. Recently, researchers at the National Tsing Hua University demonstrated that incorporating a protein, such as gelatin, into the TENG design allows for an electric output at a high relative humidity, which is even better than the electrical output generated by of TENGs in a dry environment [4]. The amino groups in gelatin allowed for a larger number of free electrons to be generated during contact of the two nodes of the TENG, which resulted in a high electrical output at a high relative humidity [4]. This is an important breakthrough that brings us one step closer to creating a biocompatible, low cost, wearable, self-powered, and easily produced TENG device for personal health monitoring.

Alginate, a biocompatible polysaccharide derived from the brown seaweed Phaeophyceae, has several of the same key amino groups as gelatin [5]. Therefore, theoretically, using alginate as a part of the TENG device should also generate a high electric output at a high relative humidity. The biopolymer layer of the TENG will be an alginate-based film. The decision to create make the biopolymer layer alginate-based rather than gelatin-based is due to the many properties that alginate has, which make it ideal for biomedical applications. In fact, alginate has already been used in a wide variety of biomedical applications, including everything from wound dressings to injectable hydrogels [5], [6]. Alginate's widespread use in the biomedical field is largely due to its low toxicity, inexpensive, biocompatible, and mild gelation, as well alginate hydrogels' minimally invasive properties, which allow for injection into the body in drug delivery applications [5], [6].

To maintain the user satisfaction with a wearable TENG device, such devices should also, ideally, be easy to keep clean through a quick, simple, and low-cost process. Another option is to make the wearable device antimicrobial, so that the user does not need to do much maintenance for the device. Logically, creating a new TENG device that is wearable, self-

powering, and biocompatible, as well as antimicrobial, would be highly desirable. Silver nanoparticles' antimicrobial properties have shown to be successful in exterminating common strains of bacteria such as S. aureus and E. coli [7]. So, to achieve the antimicrobial component of the TENG device, silver nanoparticles will be added to the biopolymer layer of the TENG. Using alginate and silver nanoparticles, we can create a wearable TENG device that is biocompatible, self-powering, and antimicrobial [1], [5], [7].

Introducing the antimicrobial aspect to TENG devices also allows for increased usability of a wearable device, especially for chronically ill patients who are physically too weak to regularly clean devices used. An antimicrobial and biocompatible TENG device would also allow for prolonged wear of the device without any user fears of developing a dermal infection or skin irritation. This is especially significant because dermal infections could further complicate matters for people with chronic illnesses or those that are taking certain medications, such as immunosuppressant drugs. Based on the preliminary data from our current work, this surface bioengineering on TENGs project is practical, important, and urgently needed.

The purpose of this project was to manufacture a wearable, alginate-based TENG device that is self-powering, biocompatible, and antimicrobial. There were three main goals for this research project: 1) To add glycerol, a plasticizer, to the biopolymer films to make the films stronger; 2) Experimentally determine which glycerol concentration within the biopolymer film would generate the highest voltage (V), current (I), and amount of electric charge (Q); and 3) To test films made from different concentrations of silver nanoparticles, alginic acid, and glycerol to experimentally determine which solution(s) will generate the highest voltage, current, and amount of electric charge for the TENG device.

Materials and Methods

Fabricating Biopolymer Films without Silver Nanoparticles

We created biopolymer films from different concentrations of silver nanoparticles, alginic acid, water, and glycerol for the fabrication of the triboelectrification layer of the TENG. First, 3 g of alginic acid, in powdered salt form, were dissolved in deionized water, under constant stirring at 70 °C, until completely dissolved. Then, different concentrations of glycerol were added into the alginate solution to create solutions with glycerol concentrations ranging from 0 M to 0.125 M. The specific concentrations of glycerol tested were 0 M, 0.015625M, 0.03125M, 0.0625M, and 0.125 M. Next, the new solution containing glycerol was stirred for 30 minutes, until the glycerol was completely dissipated into the original alginate solution. After creating the solution, each film was prepared by pouring 20 mL of the solution into sterile 100 mm x 15 mm petri dishes. These petri dishes were then placed into an oven to dry at 36 °C for ten hours.

Fabricating Biopolymer Films with Silver Nanoparticles

For the fabrication of the biopolymer films containing nanoparticles, the silver nanoparticles were prepared by reducing the silver precursor AgNO3 using sodium alginate and distilled water. The solution of sodium alginate and distilled water was created following the steps listed above, and then, to synthesize the silver nanoparticles, varying amounts of silver precursor were added to the existing alginate solution. This solution was then stirred continuously at 80 °C for sixty minutes. Different concentrations of silver precursor were added into the alginate solution for optimization, each at a volume of 10 μL. The specific concentrations we examined were 10 mM, 25 mM, 50 mM, and 100 mM solutions of silver

precursor in distilled water. After creating the solution, each film was prepared by pouring 20 mL of the solution into sterile 100 mm x 15 mm petri dishes. These petri dishes were then placed into an oven to dry at 36 °C for ten hours.

Manufacturing TENGs

TENGs are typically made from two separate nodes, and the energy is produced when one node contacts the surface of the other node. Each node consists of different layers of material, though each node's base layer was a 4 cm x 4 cm of 0.125-inch-thick piece of Polymethyl methacrylate (PMMA) for our experiments. Then, a sheet of aluminum foil with a thickness of 2 mm was taped onto the each of the two PMMA layers, with the aluminum foil completely covering one side of each base layer. From here, one node was topped with a layer of Polytetrafluoroethylene (PTFE), while the other node was topped with a layer of the biopolymer film we fabricated. PTFE and the film we fabricated served as the two triboelectrification layers of the TENG device, while the aluminum layer underneath served as the conductive layer. The assembly of the two nodes of the TENG device is depicted in Figure 1b below.

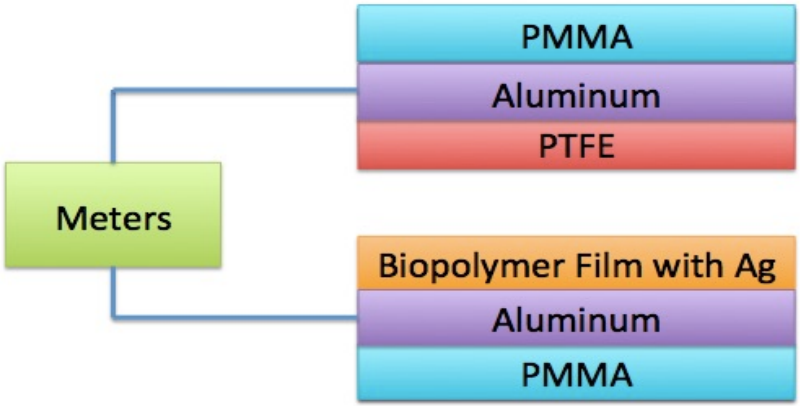

Figure 3: The figure above shows the proposed assembly of the two nodes of the TENG device. The biopolymer film contains both silver (Ag) nanoparticles and alginate.

Linear Motor Measurements

In order to characterize the performance of the TENG device, we used a linear motor to control the contact-separate experimental parameter. Essentially, the linear motor ensured that the distance between the two TENG nodes was held constant throughout the experimental trial. We set the speed of the linear motor to be 1 m/s, and both the acceleration and deceleration to be 1 m/s^2 for all of the experiments. With separation distance defined as the distance between the two nodes of the TENG when fully separated, we tested the separation distances of 5 mm, 10 mm, and 20 mm for each film to discuss potential relationships between separation distance and electrical performance. To control for any possible degradation of the biopolymer films over time, each day, we only created the films that we would use for the linear motor measurements the next day. We created solutions of alginate with deionized water, which then are dried into films, and used in the TENG design as the layer on top of the conductive layer of aluminum. An aluminum sheet was cut and taped onto the 4 cm x 4 cm piece of Polymethyl methacrylate, or PMMA. Next, the dried film was layered on top of the aluminum sheet, constituting one node of the TENG. The other node was created by layering a piece of Polytetrafluoroethylene, or PTFE, on top of the aluminum sheet.

Next, the two nodes were fixed to the linear motor using foam interface tape. Then, the nodes were wired to the electrometer (6514 system electrometer from Keithley), to measure the voltage output of the synthesized biopolymer film. The electrometer was then connected to a NI (or National Instruments) BNC-2120 board, before being connected to the computer board. The electrical output was read using a pre-written Labview code that acquired the signal readout from the computer board. We took measurements (V, Q, I) of each of the biopolymer films using the linear motor, the system set-up mentioned previously, and a pre-written LabView code. We then

exported the experimental data into Microsoft Excel and created time vs. voltage, time vs. current, and time vs. amount of electrical charge graphs for each biopolymer film.

Results

To examine the results of this research project, we looked at the trends observed from the data collected. One aim of our project was to examine the correlation, if any, between separation distance and voltage output, with separation distance defined as the distance between the two TENG nodes when mounted on the Linear Motor. Another goal was to determine the biopolymer film that would generate the highest voltage, current, and amount of electrical charge. With this goal, we distinguished that voltage output was the most crucial evaluation of electrical capacity, so we based our criteria mainly upon voltage.

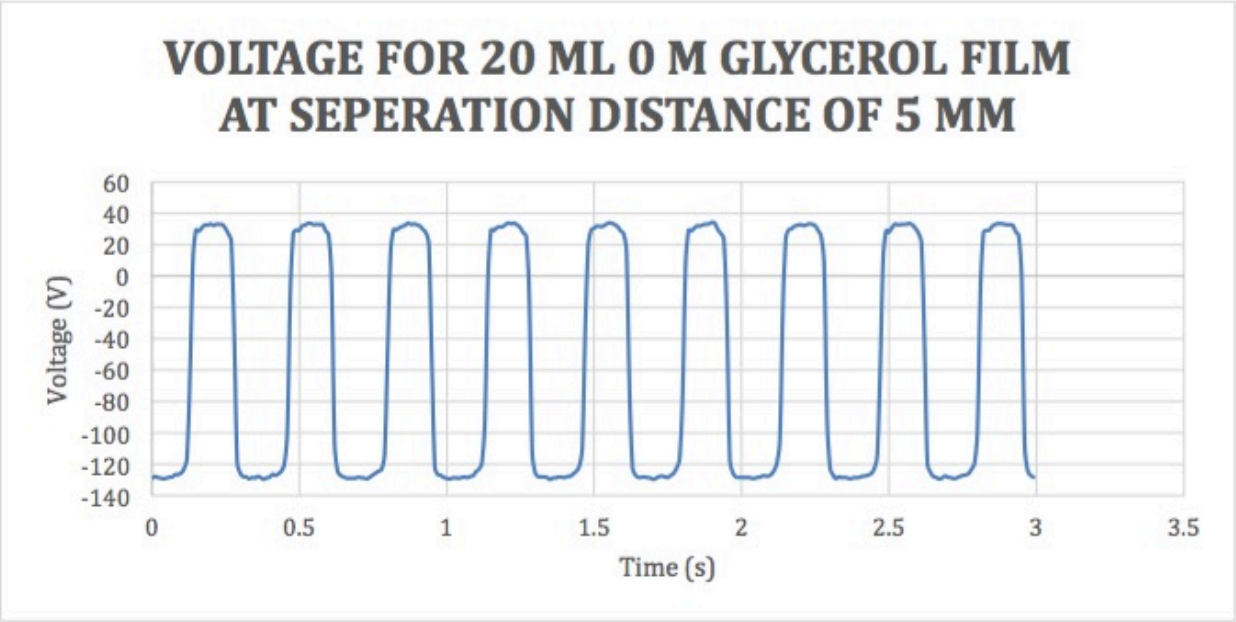

Figure 1b: Above is a graph of voltage vs. time for a 20 mL glycerol film at the separation distance of 5 mm. This particular biopolymer film generated a voltage range of 165 V.

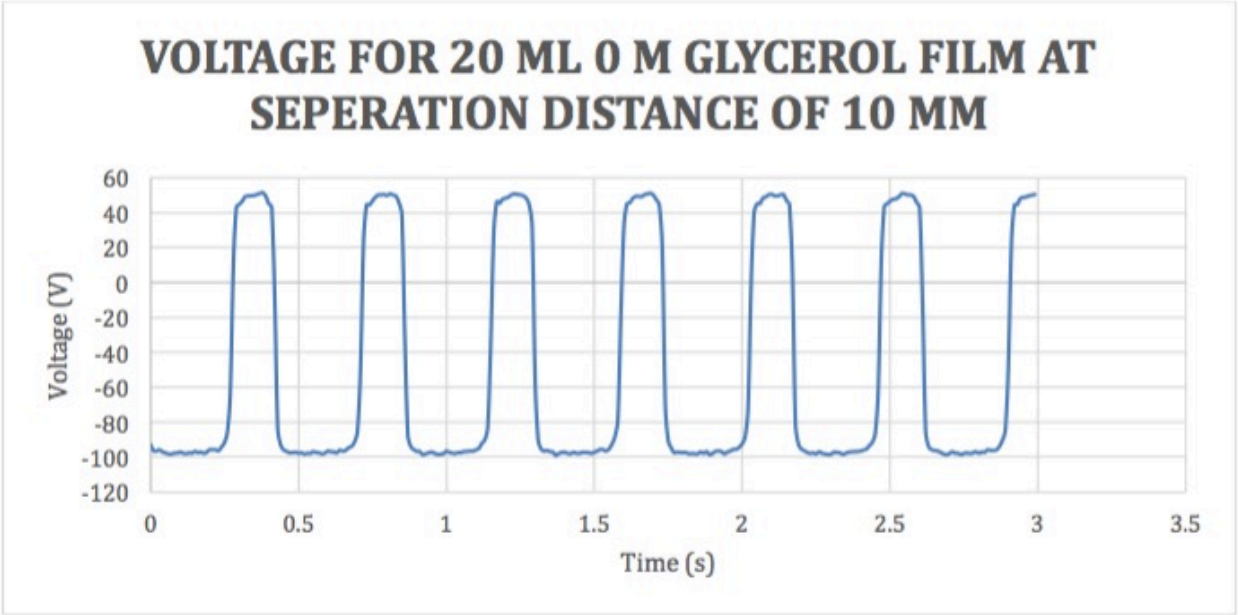

Figure 1c: Above is a graph of voltage vs. time for a 20 mL glycerol film at the separation distance of 10 mm. This particular biopolymer film generated a voltage range of 146 V.

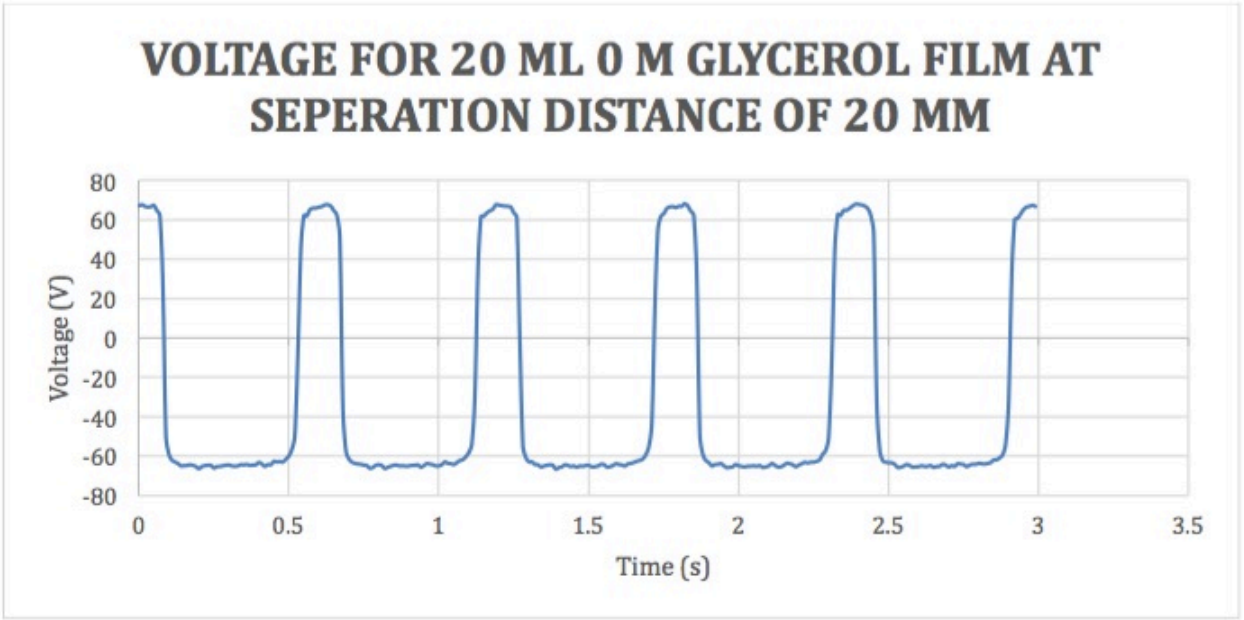

Figure 1d: Above is a graph of voltage vs. time for a 20 mL glycerol film at the separation distance of 20 mm. This particular biopolymer film generated a voltage range of 130 V.

It is important to note that in Figures 1b, 1c, and 1d above, the peaks in the graphs correspond to contact between the two nodes of the TENG while the valleys correspond to separation of the two nodes. An interesting phenomenon observed with the 0 M glycerol films was that as separation distance between the two TENG nodes increased, the voltage output decreased. This trend is significant because it is unique to the 0 M glycerol films.

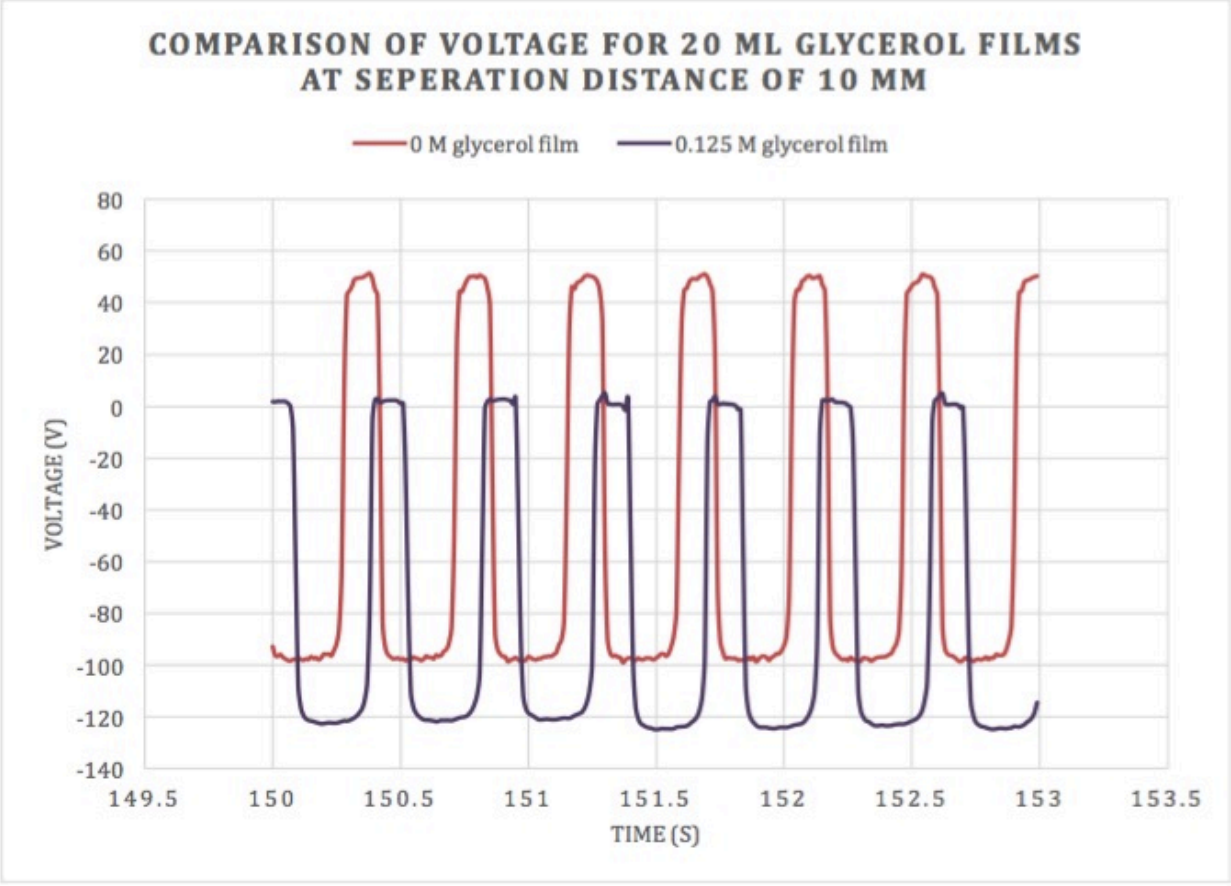

Figure 2: The figure above shows the differences in voltage ranges between the alginate-based biopolymer films without glycerol and the films with the highest concentration of glycerol (0.125 M glycerol).

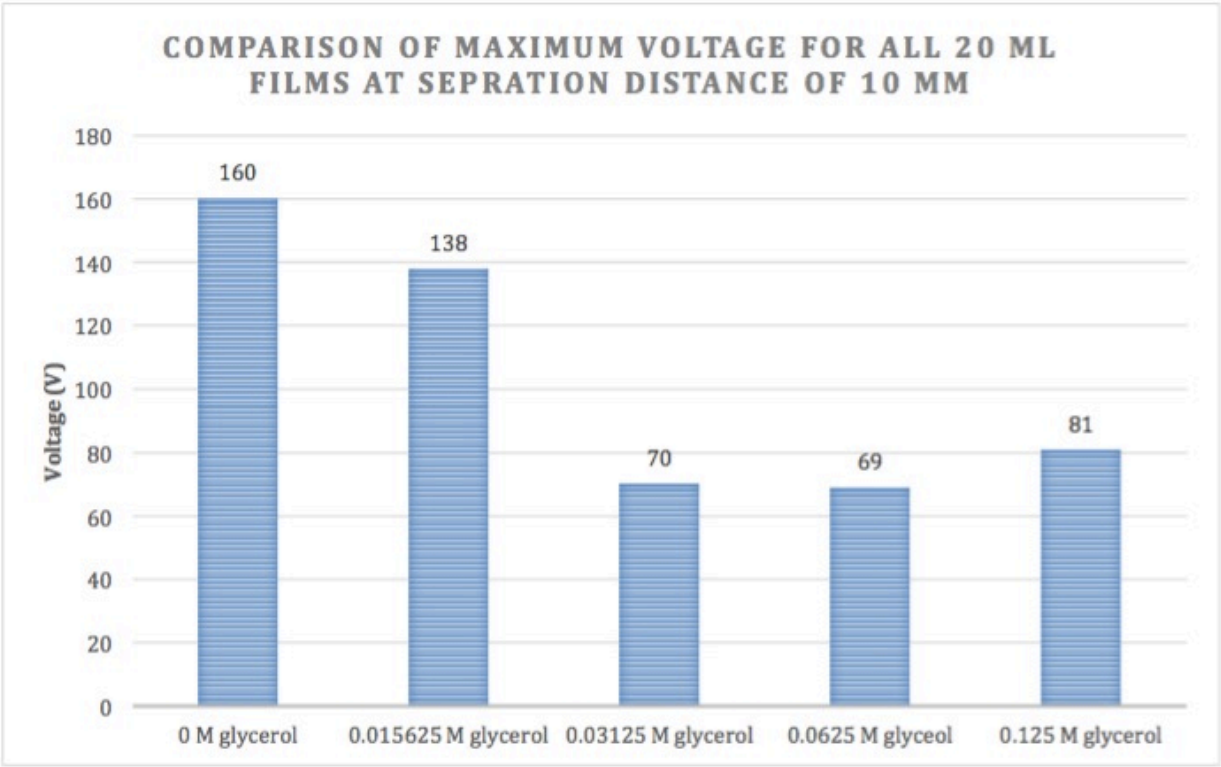

Figure 3: Above is a graph depicting the maximum voltage output range for each 20 mL film at separation distance of 10 mm. From the figure, we can see that the 0 M glycerol films generated the highest voltage output, and the 0.0625 M glycerol film generated the lowest voltage output. It is also interesting note that the 0.015625 M glycerol film generated the highest voltage output out of all of the films containing glycerol.

An interesting trend we noted was that the general decrease in maximum voltage output increases with amount of glycerol added – with the exception of the 0.125 M glycerol film. When testing the TENG devices, we noticed that films with higher glycerol concentrations were less brittle, more flexible, and highly adhesive to other surfaces. In fact, the larger the glycerol concentration was in the film, the more adhesive the film was. The highly adhesive nature of the films with large amounts of glycerol created an interesting phenomenon in which there were

larger spikes in voltage, current, and amount of electrical charge that directly corresponded to the biopolymer film adhering to the PTFE momentarily during experimentation. This phenomenon may serve to explain why the 0.125 M glycerol film did not follow the general trend as seen above in Figure 3.

When glycerol was added to the biopolymer films, a different trend was observed with respect to the separation distance that produced the highest voltage output. Instead of 5 mm separation distance generating the highest voltage output, as observed in the 0 M glycerol films, for films with glycerol, we saw that the 10 mm separation distance generated the highest voltage output. In Figure 4 below, we can see that the 10 mm separation distance generates the highest voltage output of 138 V for the 20 mL 0.015625 M glycerol film. We are only examining the 0.015625 M glycerol film here because this concentration of glycerol produced the highest voltage output in all films that contained glycerol, as shown above in Figure 3.

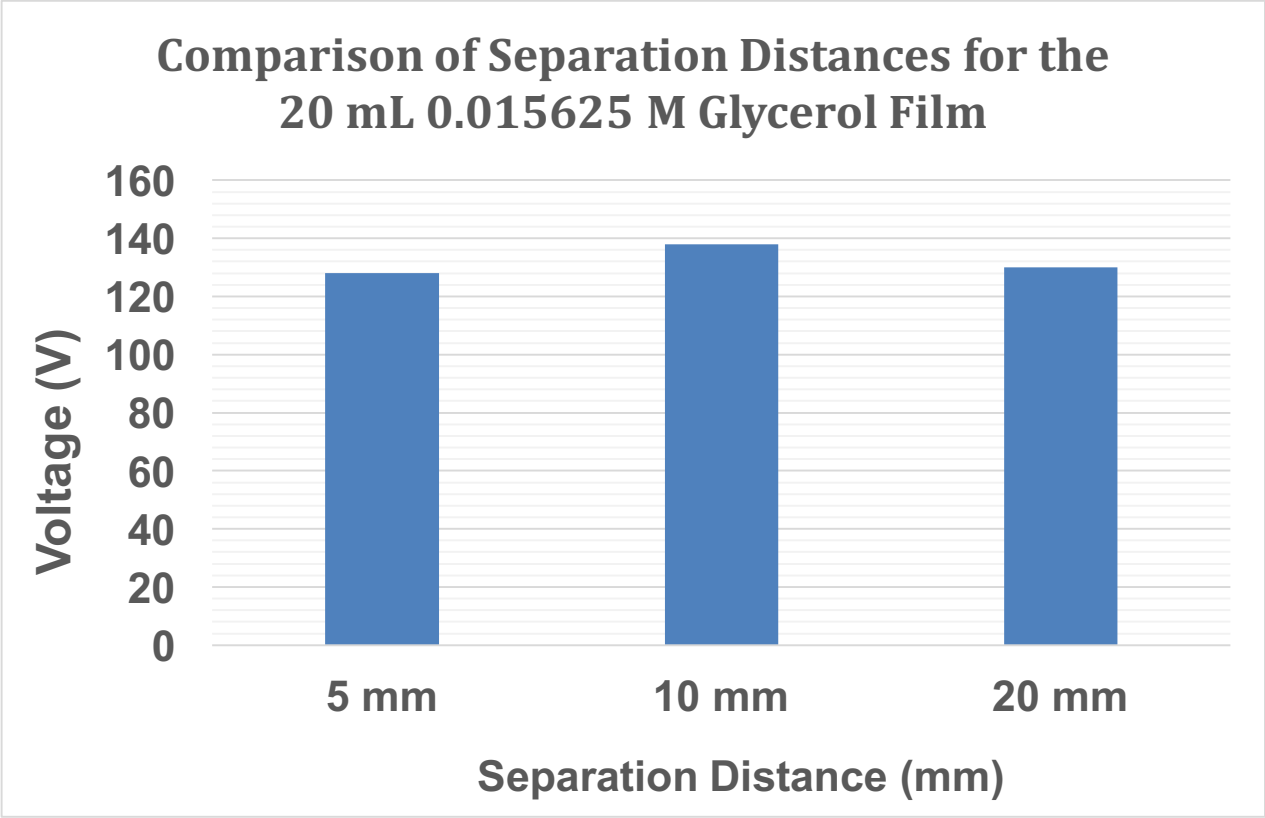

Figure 4: Above is the comparison of maximum voltage output range between the three separation distances tested for the 20 mL 0.015625 M glycerol film. It's clear that the 10 mm separation distance generates the highest voltage output.

Discussion

In our experiments, we saw that alginate-based biopolymer films constructed without glycerol (0 M glycerol films) generated the highest voltage output. The biopolymer films without glycerol were brittle in comparison to even those with the lowest glycerol concentration. Glycerol's properties as a plasticizer served to strengthen the films that contained it, making the films with glycerol less brittle, more ductile, and stronger than those without it. However, the strength of the films with glycerol came with a tradeoff – adding glycerol resulted in lower voltage outputs, with a direct correlation between decreasing voltage output and amount of

glycerol added to the films. In our data, we saw the trend that increasing glycerol concentration resulted in decreasing voltage output. Though the films with the lowest glycerol concentration of 0.015625 M only experienced a small decrease in voltage, the films with the highest glycerol concentration of 0.125 M has a significant decrease in voltage when compared to the 0 M glycerol films. The difference in voltage between the films with 0.015625 M glycerol and the 0 M glycerol films was 22 V, while the difference in voltage between the films with 0.125 M glycerol and the 0 M glycerol films was 79 V.

However, despite the fact that 0 M glycerol alginate-based biopolymer films generate the highest voltage output, we must acknowledge the brittleness of the 0 M glycerol films. Since brittle films break easily, 0 M glycerol films are not a durable option and realistically, can only be used for TENGs in certain controlled environments. To further explore options to strengthen the alginate-based biopolymer films, we examined the affect that Calcium Chloride (CaCl2) would have on the films. Calcium Chloride has shown to cause gelling when in contact with alginate solutions [3]. We believed the gelling would serve to strengthen the films, in a similar manner as the addition of glycerol strengthened the films. To do so, we created biopolymer films using the materials and methods described above, and then sprayed the films with a 1 M CaCl2 solution prior to placing the films into the oven.

Similar to the effect of adding glycerol, adding calcium chloride to our films resulted in a decrease in voltage output, though the decrease in voltage with films with calcium chloride was significantly higher than those with glycerol. The maximum voltage generated by a film containing calcium chloride was only 75 V, which is much too low to be of use in most practical applications. Due to the sharp decrease in voltage between the films with calcium chloride and those without, we did not explore the effects of calcium chloride on alginate-based biopolymer

films further. Additionally, we found that films with calcium chloride appeared stronger and thicker than those without it, but unfortunately, were still brittle. This was an important distinction between the films with calcium chloride and those that contained glycerol – the glycerol-containing films were stronger and less brittle while the films with calcium chloride were stronger but still brittle. Therefore, we concluded that alginate-based biopolymer films with calcium chloride were not a good option for TENG devices with user interaction, such as biomedical devices.

From our experiments, we have successfully distinguished the biopolymer film that is both the most durable and generates the highest voltage output – the 20 mL 0.015625 M glycerol film. Through our evaluation of different separation distances, we also identified 10 mm to be the best separation distance between the two TENG nodes in order to generate the highest voltage, current, and amount of electrical charge for alginate-based biopolymer films containing glycerol.

Future Work

Since we have successfully isolated the biopolymer film that is the most durable, and that generates the highest voltage output, our next step is to explore the effects silver nanoparticles will have upon our biopolymer films. In the Fall 2017 semester, I plan to work with Dr. Yi-Cheng Wang to explore the effects of adding silver nanoparticles to the 20 mL 0.015625 M glycerol film. The silver nanoparticles will be prepared by reducing the silver precursor AgNO3 (from Sigma-Aldrich) using sodium citrate (from Sigma-Aldrich). Different amounts of silver nanoparticles will be added into the alginate-glycerol solution for optimization, starting at a volume of 10 μL. We were also unable to use an e-beam evaporator to deposit aluminum onto

the nodes this summer due to equipment issues. In the next phase of this project, we plan to create the aluminum layer by depositing aluminum with a thickness of 100nm onto each of the two PMMA layers through an e-beam evaporator.

Although we tested both 20 mL and 30 mL films for each of the glycerol concentrations, we were not able to reach a conclusion that favored any one thickness of biopolymer film over the other. However, it was interesting to note that the general trend we observed was that 30 mL films were often more brittle than 20 mL films. This trend was especially true for films with lower amounts of glycerol. Since the 30 mL films were more brittle, most broke during the TENG manufacturing process, and so we were unable to test these films. A future step would be to more closely examine the role that film thickness plays in voltage output, current, and amount of electrical charge generated.

Professor Wang's lab has recently acquired a Fourier transform infrared spectroscopy (FT-IR) machine, which can characterize polymer surface functional groups [8]. FT-IR machines are able to identify the presence of specific functional groups and to detect the molecular makeup of a particular sample [9]. We plan to use the FT-IR to examine the surfaces of the films containing calcium chloride to better understand the brittleness of these films. The FT-IR would also help us determine the reason behind the decrease in voltage output experienced when glycerol is added to the alginate-based biopolymer films.

However, we have not conducted in-depth data analysis yet. After we experimentally determine the effect that the addition of silver nanoparticles has, we will use paired t-tests to determine significance. Specifically, we will be comparing the differences, if any, in voltage, current, and amount of electrical charge produced in alginate-based biopolymer films versus alginate-based biopolymer films with silver nanoparticles.

However, from our preliminary data, we predict that the voltage, current, and amount of electrical charge will increase with respect to concentration of silver nanoparticles. From the biopolymer films with silver nanoparticles that we have tested thus far, this trend has been followed. This linear trend, if it continues in repeat experiments, would be highly significant for the field in terms of potentially creating a new triboelectric material.

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