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Investigation of Surface Charge using Faraday Bucket Measurements: Analysis on Electrospun Polyvinylidene Fluoride Fiber Mats

Ryan Kantenwein
rhk9@zips.uakron.edu

The University of Akron:

College of Engineering & Polymer Science

Department of Chemical & Biomolecular Engineering

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Analysis on Electrospun Polyvinylidene Fluoride Fiber Mats

Author(s)

Ryan Kantenwein

Prof. George Chase, Project Faculty Advisor

Mr. Harshal Gade, Graduate Student Mentor

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1. Executive Summary

Polymer materials and their chemical properties allow for new research into advanced products for use in a variety of markets. Measuring surface charge with instruments such as a Faraday bucket provides insight on how polymers can be utilized in life-saving day to day applications. Biomedical personal protective equipment, such as face masks, can utilize polymeric materials to filter viral microparticles – an essential device during a global pandemic. Electrospinning is a viable polymer processing method which uses the piezoelectric property of polyvinylidene fluoride to create charged nanofiber mats. These mats are tested within the Faraday bucket instrument and can later be used as the basis in a filter apparatus. Many filtration devices utilize a physical protective barrier against particles, however; polymers such as PVDF can provide an electrical interactive barrier in tandem with a physical one to improve performance.

PVDF Kynar 761 is tested at 10 wt% in solution with solvents of dimethylformamide and acetone at a 1:1 ratio. These nanofiber mats are bombarded with NaCl aerosolized particles in a TSI 8130 instrument. After salt loading, Kynar 761 at 10 wt% increases surface charge in all regions of the nanofiber mats tested. PVDF Kynar 761 and MG-15, another variant of PVDF, are tested at 18 wt% and show a development of surface charge after the electrospinning process. Neither Kynar 761 or MG-15 at 18 wt% were tested for surface charge after TSI 8130 processing.

The Faraday bucket proves to be an affective instrument to measure the voltage and associated surface charge on the nanofiber mats. Kynar 761 and MG-15 are potential polymeric materials which could be utilized to assist in the filtration performance of biomedical safety devices. The electrical surface interactions with foreign particles to the human body may help in preventing viral contaminants from entering the airway. Another PDVF variant, Kynar 741, does not process correctly at 18 wt% and could be another potential polymeric material, yet not surface charge data is available for this investigation.

This research investigation provides an academic insight into the chemical properties of new polymer materials for use in several industries and applications. Other polymer processing equipment besides electrospinning can be used industrially to create beneficial products which continue to advance modern technology. A unique perspective of undergraduate research, chemical engineering topics, and material science is incorporated into this investigation. Further research can focus on any of these related topics including additional investigation into Kynar 741 at varying concentrations and other variants of polyvinylidene fluoride. Also, more piezoelectric polymers should be researched to act as a comparison to the potential filtration effects provided by PVDF.

2. Introduction

2.1 – Piezoelectricity of Polyvinylidene fluoride

Polymer materials possess unique chemical structures which influence the strength and consistency of their mechanical and electrical properties. Polyvinylidene fluoride is synthesized in a particular method to take advantage of its strong, piezoelectric property in the β-phase [2]. This configuration provides a reliable dielectric polymer material which is difficult to reverse, or breakdown, once mechanical stresses are applied. Permanent electric dipoles maintain surface charge easier in the b-phase due to alternating $-CH_2$ and $-CF_2$ groups along the polymer backbone [1]. The piezoelectric property of these polymers motivates the desirability of electrospinning as a popular method to produce new, advanced materials. Electrical forces, generated by a high voltage supply, influence free ion charges within the polymer solution. These forces overcome the surface tensions of the polymer droplets and jet, or splay, onto the grounded collection net. An electrical pathway is created from the positive tip of a syringe to the ground of the net resulting in a polarized structure of the polymer. Stretching of the solution through the electric field causes mechanical stresses to the chemical structure and thus rearranges the free ions into dipoles creating a new, polarized state [3]. Gade also demonstrated that parameters such as fiber diameter, pore size, surface charge, and thickness are essential when synthesizing a nanofiber, electrospun mat.

2.2 - New Filtration Products

New techniques, instruments, and materials to electro spin polymer solutions are utilized to manipulate various chemical and physical properties for end of use applications. Developments in electrospinning have altered parameters such as material selection, nanofiber diameter, orientation, density, and distribution. Each combination of these parameters can result in a polymer product for uses in several filtration applications. The electrospinning conditions for a PVDF solution, modeled by the setup tested in **Figure 3.1** can create charged polymer nanofiber mats. The mats contain surface charge distributed over their surface due to the electrical properties such as piezo, pyro and ferroelectricity originating from the chemical structure of PVDF [1]. PVDF in form of as-spun and functionalized fibers find use in variety of applications such as aerosol filtration, water-diesel separation, and water desalination applications [2,3,4].

3. Experimental Methods

3.1 – Electrospinning of Fiber Mats

Each test variable in question must commence with the initial creation step of the polymer solution. PVDF powder is mixed in a weight percentage ratio with two solvents – dimethylformamide and acetone in equal ratios to themselves. This solution is prepared with a hot plate and stirred with a magnetic stir bar at 70°C for 15 minutes. The solution should be translucent in color when the 15-minute heat and mixing is applied. This polymer solution is ready after some cooling for the electrospinning process. A syringe is filled to the 5mL mark with solution, and a male and female attachment connects an extension tube to the tip of the syringe needle. The electrospinning apparatus needs to be checked first to ensure all components are present and can be isolated when powered on. These components are the following: an adjustable motor/controls, a collection drum, a PVC rod and stand with drilled holes, a voltage generator, a calibrated syringe pump, and aluminum foil. Once all the components and supplies are ready for the electrospinning process, the syringe can be placed in the pump, secured, and set in range of the PVC pipe with holes. A PTFE 1/8 inch tube connects the syringe to a steel needle. The syringe needle is placed through one of the centered holes about 17 cm above the grounded collection drum covered with aluminum foil to ensure a consistent and even creation of the polymer fiber mat. A wire from the high voltage power supply is clipped to the needle tip to charge the needle. A ground wire is clipped to the collection drum via a wire connected to its center shaft. Once completed, power to the drum motor, voltage generator, and syringe pump can be turned on in that order. The voltage applied to the needle is about 27 kV but the actual voltage is adjusted until the electrospinning process begins, and solid fibers collect onto the drum as a fiber mat. The fibers collect in a way that closely follows the path of the electric field between the needle and the collection drum. Each syringe of 5 mL can spin in about 1 hr. Depending on the desired basis weight of the mat sample up to two syringes may be required and applied in sequence. After spinning, the aluminum foil with the mat sample still attached is placed into an oven at 70°C for 3 hours to evaporate of any remaining solvent in the mat sample.
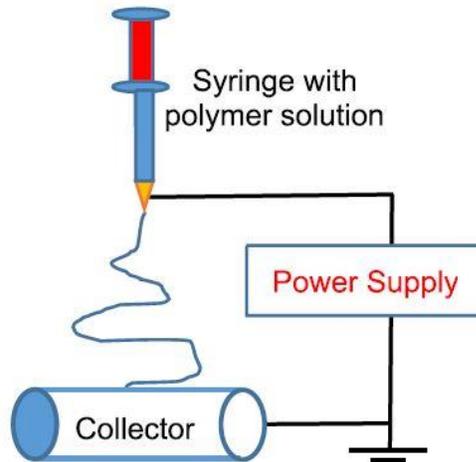
Figure 3.1 *– The basic electrospinning set up schematic for creation of polymer nanofiber mats of varying polymer solutions [5].*

3.2 - TSI 8130 Testing

   Aerosolized NaCl particles were bombarded through the nanofiber mats to assess the filtration performance of samples. The TSI 8130 machine vaporizes an NaCl solution under heat for 15 minutes as the machine builds pressure to allow a controlled, set flow through the sample. After a blank, wire mesh orifice has been allowed flow to pass through, the baseline standard is calibrated into the equipment. A nanofiber mat can be inserted over the wire mesh and the orifice to allow flow to contact the sample and take readings of pressure drop and penetration. This information is recorded and analyzed to assess the performance of NaCl particles passing through and being captured onto the nanofibers.
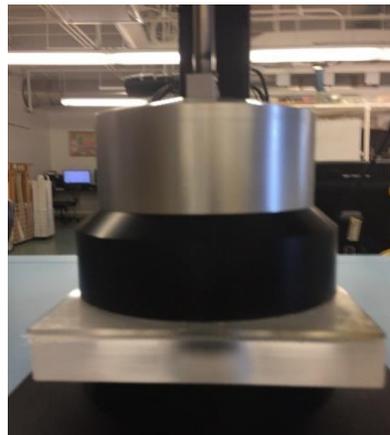

Figure 3.2 *- Filter holder positioned on filter tester as clamped by pneumatic cylinder.*

3.3 - Faraday Bucket Testing

The Faraday Bucket readings are an insight to the electrical surface charge readings and interactions dispersed throughout the area of the nanofiber mat. Samples, after the creation step, need to be sealed in aluminum foil and within an anti-static bag to ensure isolation of charges from the outside environment. When Faraday Bucket testing commences, a sample is taken out of its anti-static bag and attached to a clothespin by a pre-cut tab. An electrometer is turned on to maximum sensitivity and tared to zero voltage. The sample is lowered by activating a switch which drives a motor and linear actuator type arm into the inner metallic bucket. The surface charge induces a voltage in the system and slowly degrades back to a zero-voltage reading over time. The initial voltage is recorded, and a stopwatch is activated at the moment the sample has fully passed into the bucket and cage. The timer is monitored carefully, and a time stamp is recorded each instant of a drop in voltage potential on the electrometer. Data from this experiment is the main contributor to determining average surface charge over the mass of the fiber mat. Surface charge can vary based on multiple factors such as basis weight, fiber diameter, method of creation, etc. All these parameters, dimensions, and outlying variables are each a hypothesis within the lab. Their influences on surface charge and filtration performance are what drive experiments in the lab. The details of this instrument have been published here [5].

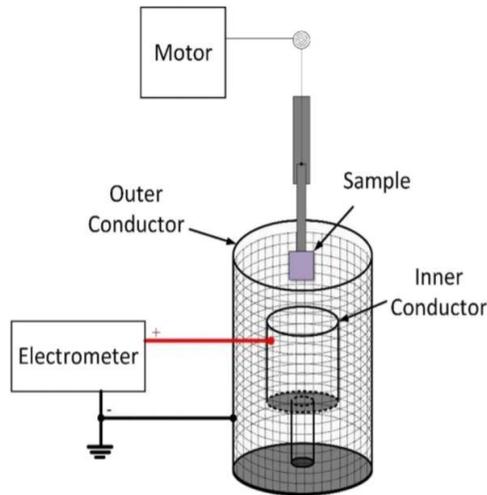*Figure 3.3 - The basic Faraday bucket set up schematic for measurement of voltage output from surface charges present on various polymer mat samples [6].*

3.4 – Surface Charge Calculation

Following Faraday bucket measurements, relating the average voltage readings to surface charge utilizing the constant capacitance of the voltmeter gives the expression:

$$Q_{avg} = CV_{avg} \qquad\qquad [1]$$

A final surface charge per mass is obtained by using this relationship and the appropriate unit conversions to nC/g. A natural log plot of $-\ln(V/V_o)$ versus time (seconds) provides a visual to the initial voltage readings and the diminishing voltage over time. The linear fit of this plot is used to provide a time constant for a sample, τ, which is the defined as the inverse of the slope of a best fit line.

4. Results

4.1 – Base 10 wt% Kynar 761 Fiber Mat Charge

The previously described standard procedure of electrospinning for polymer mat creation in **Section 3.1** presents a non-uniform splay pattern. A PVDF, polymer solution consisting specifically of 10 wt% Kynar 761 (with 1:1 ratio dimethylformamide/acetone solvents) is splayed onto the collection aluminum medium. This pattern is observed across the distribution of surface charge along the entire surface area of the mat. *Figure 4.1* displays the higher concentration of surface charge in the center of the polymer mat which, during initial creation, rotates directly under the syringe tip of polymer solution.
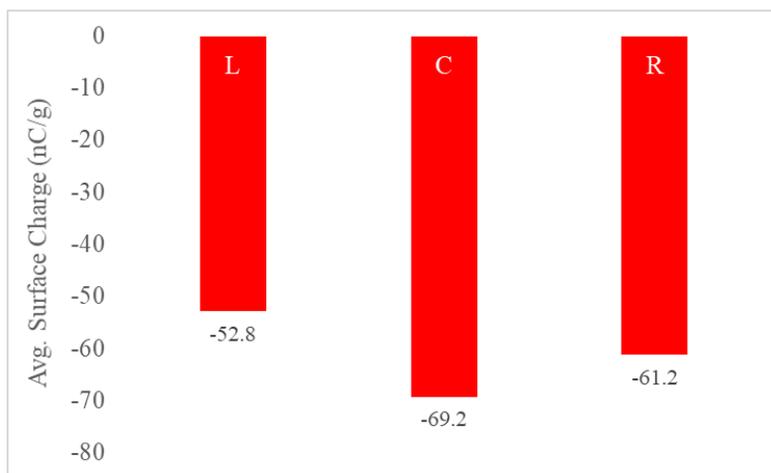

Figure 4.1 – Surface charge accumulates near the center regions of the 10 wt% Kynar 761 polymer mats as demonstrated by a higher charge of -69.2 nC/g compared against lower calculated charges -61.2 and -52.8 nC/g for right and left regions, respectively.

Each of the results displayed in *Figure 4.1* are average charge per mass of sample tested within the Faraday bucket instrument. Voltage responses are observed from an electrometer and utilized to calculate the data provided above. These data provide a baseline or control prior to bombarding samples with aerosolized NaCl particles to see a response in voltage and hence surface charge.

Table 4.1 – *The pre-salt loading, 10 wt% Kynar 761 samples are displayed in the table below. Referencing the mathematical operations in **Section 3.4** above, an average surface charge in nC/g per sample is summarized. Initial maximum voltage readings are utilized in these calculations along with a fixed voltmeter capacitance and time constant. A fourth sample for the "right" average values is not displayed as experimental data only exists for three samples.*

Weight of sample(g)	Sample ID	Voltage Replicate reading(V)	Average Voltage(V)	Time constant (s)	capacitance (F)	Capacitance(pF)	Charge (C)	Charge(nC/g)	Average charge (nC/g)
0.037	8192020-L	-15		1429			-3.11E-09	-85.0	
0.047	8272020-L	-8	-37.0	1667			-3.11E-09	-65.9	-52.8
0.103	9222020-L	-60		2500			-3.11E-09	-30.3	
0.103	10012020-L	-65		10000			-3.11E-09	-30.1	
0.037	8192020-C	-18		1429			-3.72E-09	-101	
0.055	8272020-C	-18	-44.3	1429	8.41E-11	84.1	-3.72E-09	-67.3	-69.2
0.096	9222020-C	-64		3333			-3.72E-09	-39.0	
0.105	10012020-C	-77		10000			-3.72E-09	-35.5	
0.034	8192020-R	-15		3333			-3.81E-09	-111	
n/a	n/a	n/a	-45.3	n/a			-3.81E-09	n/a	-61.2
0.104	9222020-R	-55		3333			-3.81E-09	-36.6	
0.105	10012020-R	-66		10000			-3.81E-09	-36.2	

4.2 – 10 wt% Kynar 761 Fiber Mat Charge (Post TSI 8130)

After completing the salt loading procedure, as described in **Section 3.2**, samples are re-tested in the same manner as before with the Faraday bucket instrument. NaCl particles have attached to the nanofibers of the polymer lattice structure. Due to non-uniform loading of many trials in the TSI 8130 instrument, a similar charge-centric pattern does not appear in the data as it appears in the baseline samples.
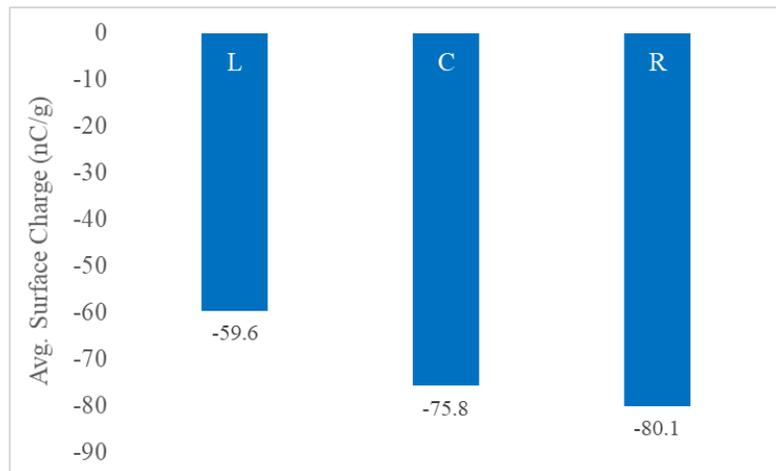
Table 4.2 - *The post-salt loading, 10 wt% Kynar 761 samples are displayed in the table below. Similar data to* **Table 4.1** *is displayed below.*

Weight of sample(g)	Sample ID	Voltage Replicate reading(V)	Average Voltage(V)	Time constant (s)	capacitance (F)	Capacitance(pF)	Charge (C)	Charge(nC/g)	Average charge (nC/g)
0.039	8192020-L	-8		833			-3.68E-09	-93.6	
0.050	8272020-L	-19	-43.8	909			-3.68E-09	-73.9	-59.6
0.103	9222020-L	-72		2500			-3.68E-09	-35.8	
0.105	10012020-L	-76		5000			-3.68E-09	-35.2	
0.038	8192020-C	-17		714			-4.12E-09	-109	
0.055	8272020-C	-22	-49.0	769	8.41E-11	84.1	-4.12E-09	-75.2	-75.8
0.096	9222020-C	-70		5000			-4.12E-09	-43.0	
0.107	10012020-C	-87		10000			-4.12E-09	-38.7	
0.035	8192020-R	-13		769			-5.07E-09	-143	
n/a	n/a	n/a	-60.3	n/a			-5.07E-09	n/a	-80.1
0.104	9222020-R	-76		5000			-5.07E-09	-48.9	
0.106	10012020-R	-92		10000			-5.07E-09	-48.1	

Demonstrated by the increase on average charge over each sample, the NaCl particles have influenced a response as expected for the 10 wt% samples.
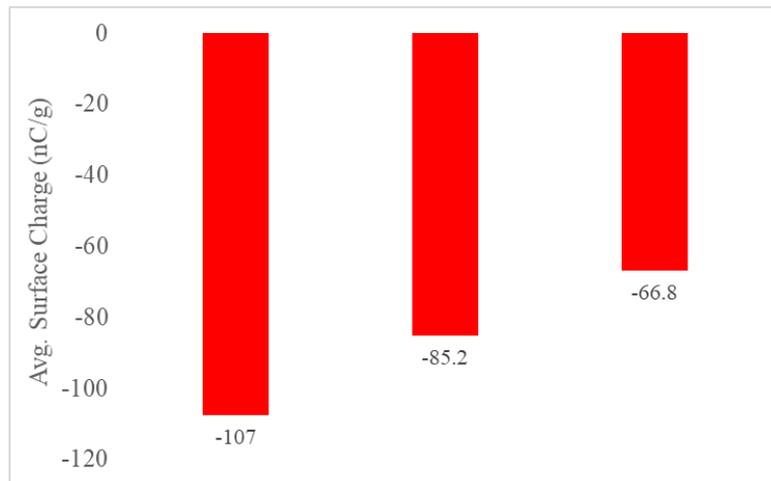
4.3 – 18 wt% Kynar 761 Fiber Mat Charge

Figure 4.3 – *Surface charge of the 18 wt% Kynar 761 polymer mats is -107, -85.2, and -66.8 nC/g for the left, center, and right regions, respectively. All regions of these samples have higher surface charge than that of the 10 wt% Kynar 761 samples.*

Weight of sample(g)	Sample ID	Voltage Replicate reading(V)	Average Voltage(V)	Time constant (s)	capacitance (F)	Capacitance(pF)	Charge (C)	Charge(nC/g)	Average charge (nC/g)
0.0156	9032020-761	-7	-23.00	1000	8.41E-11	8.41E+01	-1.93E-09	-124	-107
0.0213	10152020-761	-39		10000	8.41E-11	8.41E+01	-1.93E-09	-90.8	
0.0236	9032020-761	-8	-22.50	455	8.41E-11	8.41E+01	-1.89E-09	-80.2	-85.2
0.0210	10152020-761	-37		10000	8.41E-11	8.41E+01	-1.89E-09	-90.1	
0.0247	9032020-761	-6	-19.00	1111	8.41E-11	8.41E+01	-1.60E-09	-64.7	-66.8
0.0232	10152020-761	-32		10000	8.41E-11	8.41E+01	-1.60E-09	-68.9	

4.4 – 18 wt% MG-15 Fiber Mat Charge

Another variant of Kynar PVDF, MG-15, provides a reference point of interest due to a higher molecular weight and is sampled at 18 wt% in solution. The preparation follows that of previous samples of 18 wt% Kynar 761 utilizing the same solvents in a 1:1 ratio as before.
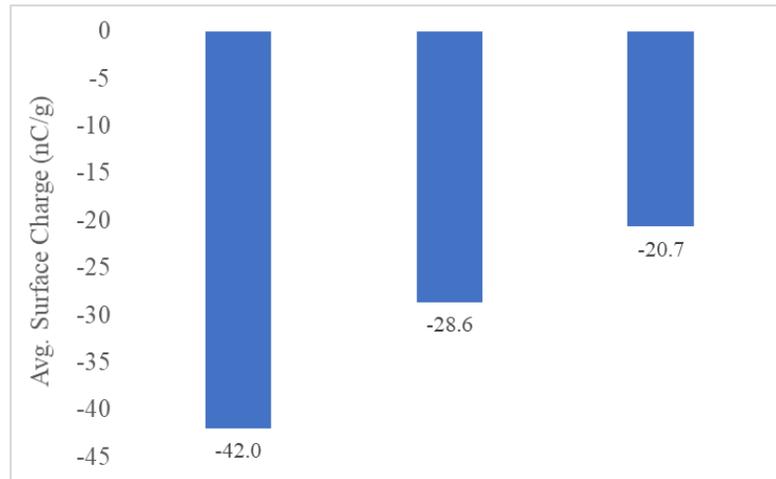

Figure 4.4 – *Surface charge of 18 wt% MG-15 polymer mats is -42.0, -28.6, and -20.7 nC/g for the left, center, and right regions, respectively. All regions of these samples have lower surface charge than that displayed in the Kynar 761 results.*

Table 4.4 – The 18 wt% MG-15 samples are displayed in the table below. A variant of the PVDF material by molecular weight, MG-15, demonstrates lower surface charge values.

Weight of sample(g)	Sample ID	Voltage Replicate reading(V)	Average Voltage(V)	Time constant (s)	capacitance (F)	Capacitance(pF)	Charge (C)	Charge(nC/g)	Average charge (nC/g)
0.0861	10122020-MG15	-43	-43.00	5000	8.41E-11	8.41E+01	-3.62E-09	-42.0	-42.0
0.1057	10122020-MG15	-36	-36.00	3333	8.41E-11	8.41E+01	-3.03E-09	-28.6	-28.6
0.1099	10122020-MG15	-27	-27.00	5000	8.41E-11	8.41E+01	-2.27E-09	-20.7	-20.7

5. Discussion

5.1 – Kynar 761 Polyvinylidene fluoride

Electrospinning a PVDF solution allows for the molecular backbone structures to respond to stresses during processing with an associated surface charge. This is observed in each of the Kynar 761 samples, as expected. Post-salt loaded 10 wt% Kynar 761 samples show an increase in surface charge as measured by Faraday bucket instrumentation. This increase is expected to be a causation of multiple possibilities including the aerated NaCl ions interacting with the charged nanofiber matrix, and the potential kinetic energy of electron collisions during salt loading [1]. By influencing the charge on pre-salt loaded nanofiber matrices, a new electrically charged nanostructure can have possible, positive effects on neutralizing or influencing other particulates passing through the mats. This is, even though not tested within the scope of this investigation, an area of filtration research utilized for several biomolecular applications.

5.2 – Kynar MG-15 Polyvinylidene fluoride

This PDVF variant with a higher molecular weight than that of Kynar 761 is a comparative reference to the 18 wt% 761 samples. The mass of each MG-15 sample is on average four times more massive than the same 18 wt% 761 comparison. As stated previously in **Section 2.1**, fiber diameter and thickness of samples significantly influence surface charge as the electrospinning process occurs. Processing a higher molecular weight material allows for more mass to hold charge therefore distributing electrical charge to more sample and lowering the overall charge per mass values.

5.3 – Effect of weight percent PDVF in solution

An increased weight percent of PVDF in solution increases the potential for more of the piezoelectric property to benefit the end product. More molecular rearrangements of alternating functional groups allow for an increased generation of surface charge as observed in the baseline Kynar 10 wt% samples in comparison to the 18 wt%

samples. There was an increase in charge for every region when processing these higher concentrated PDVF mats.

6. Conclusions

Polyvinylidene fluoride is a piezoelectric polymer which develops and maintains surface charge after electrospinning due to its chemical structure and properties. Passing aerated NaCl particulates through sample mats at constant volumetric flowrates increases surface charge in all 10 wt% Kynar 761 samples. Increasing from 10 wt % to 18 wt% Kynar 761 allows for more surface charge to accumulate on a sample. An increased mass results in a higher potential for electric dipoles to be influenced within the sample therefore assisting charge movement, storage, and consistency. 18 wt% Kynar MG-15 also develops and maintains surface charge at a lower value caused by an increased molecular weight compared to Kynar 761.

Future testing on more variants of polyvinylidene fluoride will provide insight to the best piezoelectric polymer material applied to medical filtration devices and PPE. Although inconclusive, 18 wt% Kynar 741 is another variant of PVDF which did not splay onto a collection medium in an effective manner; however, other concentrations of this variant can be explored in further investigations. In addition, form factors of polymer fibers such as yarns are currently being tested as to the effectiveness of varying geometries of PVDF nanostructures [4].

7. References

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