# A Modified Electrospinning Method for Conductive and Insulating Materials

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***Abstract*—Leaky dielectric solutions have the characteristics of quickly conducting the charges to the surface from the interior and the ability to sustain the electric field tangential to the jet surface. Therefore, perfect dielectric solutions which have no ability to conduct the charges from inside to the fluid surface or highly conductive polymer solutions which do not have the ability to sustain the electric field tangential to the fluid surface are very difficult to electrospin. The present work proposes a method for electrospining of conductive polymer solutions without adding a supportive polymer to make polymer blends. The method is demonstrated by using sodium alginate which is a biopolymer that cannot electrospin alone due to its high electrical conductivity. Furthermore, the method can be applicable to polymers with low conductivity, like silicone rubber.**

## I. Introduction

With the invention of electrospinning as a viable fiber spinning technique in the late 1930s, many researches have tried to electrospin various materials including synthetic and natural polymers, polymer blends, and ceramics. It has been generally accepted that the solution must be a leaky dielectric for a continuous and efficient electrospinning. This is because the leaky dielectric solutions have the characteristics of quickly conducting the charges to the surface from the interior and the ability to sustain the electric field tangential to the fluid surface. The dielectric properties of a liquid are primarily governed by the conductivity, permittivity, ionization, and polarization characteristics of the material and therefore, these affect significantly on the electrospinnability of a solution. Thus, it is difficult or not possible, in some cases, to electrospin solutions that are highly conductive or insulating though, the other properties of a polymer solution are in the required range for electrospining.

The use of bio-degradable polymers has been significantly increased in the recent past to minimize the environmental damage caused by the synthetic polymers. Therefore, there is a growing market for electrospun nanofibers using natural polymers with many potential applications in the areas of food, medical, and pharmaceutical fields [1]. Thus, many natural polymers such as cellulose acetate, chitin, chitosan, alginate, collagen, gela-

tin, and silk have been tried to electrospin by researches worldwide [1, 2]. However, most of the times, they have used a carrier synthetic polymer to electrospin natural biopolymers, because of their extensive polyelectrolyte behavior [1, 3-6]. Similarly, some researches have tried to electrospin conductive polymers to make highly efficient semiconductor devices such as Schottky nanodiodes. For example, Pinto et. al. have experimented electrospinning polyaniline which is a conductive polymer; however, they have only succeeded electrospinning polyaniline by making a polymer blend, mixing with polyethylene oxide (PEO) [7, 8]. In addition, to authors' knowledge, electrospinning highly insulating materials such as silicone rubber has not been carried out to-date.

Therefore, the aim of the present work is to develop a method to electrospin highly conductive or insulating materials without using a carrier synthetic polymer. Sodium alginate (SA) which is a natural bio-polymer mostly extracted from seaweeds and RTV615, a two part silicone rubber which is an insulating material were used to conduct the experiments. Scanning electron microscopy (SEM) technique was used to investigate the morphology of collected fibers.

## II. THEORY

The basic principles for dealing with electrified fluids were developed in a series of papers written by Taylor in the early 1960s [9, 10]. Later, the theory was developed further, and it became accepted that the electrospinning process is governed by a variety of forces which include Coulomb force between the charge particles on the jet surface, the electrostatistic force due to the external electric field, viscoelastic force due to the viscosity of the solution, surface tension force, gravitational force, and air drag force due to air friction [11]. The entire electrospinning process including Taylor cone formation, the straight jet portion, and the whipping jet region is highly dependent on the Coulomb force between the charges on the surface of the fluid and the force due to the external electric field. However, the formation of the Taylor cone is governed mainly by the electrostatic force created by the surface charges with the application of an external electric field that can be divided into two components namely tangential field ($E_t$) which is tangential to the fluid surface and normal field ($E_n$) which is normal to the fluid surface as shown in Fig. 1. On the other hand, both Coulomb and electrostatic forces influence the elongating and thinning of the straight jet portion. Thus, the Coulomb force is the main factor in the whipping instability of the jet [11].

In an uncharged ionic solution, there are same numbers of positive and negative carriers in each volume segment of the solution [11]. If the liquid has a sufficiently high electrical conductivity, with the application of an external electric field, the positive and negative ions in the polymer solution have a tendency to move in opposite directions. Therefore, the excess charge which is the difference in the number of positive and negative ions in a particular volume segment is simply considered as its charge [11]. This would form a charged layer at the liquid-gas interface and the electrochemical equilibrium of the charge carriers is achieved by making the charge distribution such that the field is normal to the liquid surface [12].

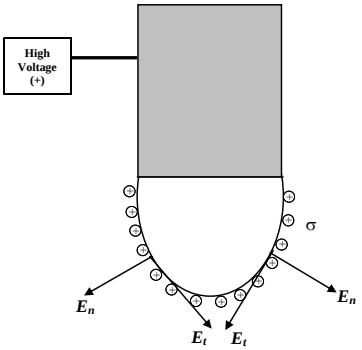


Fig. 1: Representation of tangential and normal electric fields at the fluid surface with the application of high voltage.

As shown in Fig. 1, if the surface charge density at the fluid surface is σ, simply the tangential electric stress ($\tau_{es}$) can be calculated as follows.

$$\tau_{es} = \sigma E_t \tag{1}$$

It is this tangential electric field together with gravity disturbs the equilibrium state of a fluid droplet or jet. As a result, a liquid jet that is pulled down under the action of above forces accelerates and decreases the jet radius. However, the influence of gravity is negligible [11]. Therefore, the most influential parameters for jet formation are the surface charge density and tangential electric field at the fluid surface. Thus, variation in the solution conductivity affects significantly $\tau_{es}$. Fig. 2 shows a variation in the tangential

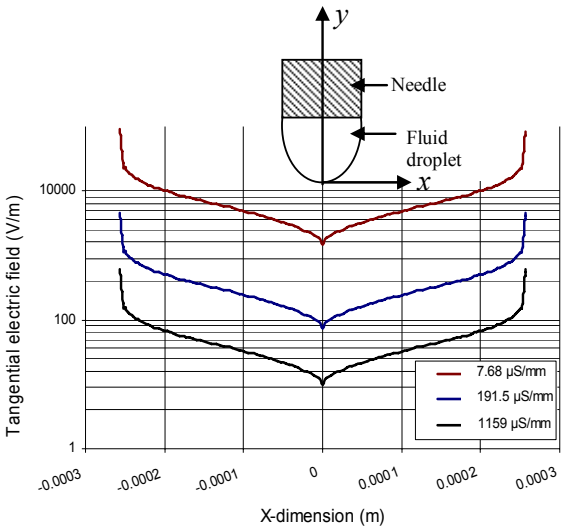


Fig. 2: Simulated tangential electric field distribution along the surface of the fluid droplet for different conductivities.

electric field at the fluid surface of a solution with the increase in solution conductivity from 8 μS/mm to 1160 μS/mm. It can be observed that the tangential electric field decreases appreciably when the conductivity of the solution increases by several orders. This finally results in the reduction of tangential electric stress, influencing the jet formation from the Taylor cone. On the other hand, as shown in Fig. 3, if it is a highly insulating liquid, there are not enough free carriers at the fluid surface since it is very difficult to separate the charges. This would result in the reduction of surface charge density at the fluid surface; hence, $\tau_{es}$. Therefore, for a jet ejection from the Taylor cone, the solution must be a leaky dielectric solution which has the ability to quickly conduct the charges to the surface from its interior and sustain the electric field tangential to the fluid surface.

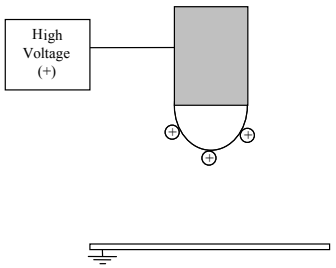


Fig. 3: Representation of the presence of surface charge at the fluid surface of an insulating liquid.

## III. EXPERIMENTAL

### *A. Experimental Setup*

Fig. 4 illustrates the modified experimental setup that was used to perform the electrospinning experiments. Polymer solutions were fed through a syringe needle arrangement at a constant rate of 0.05 ml/min from a syringe pump, resulting in the formation of a drop of polymer solution at the needle tip. A needle of AWG of 19 inner diameter was used and Spellman high voltage DC power supply was used to apply the high voltage between the needle and the collector plate. The plate was heated during the electrospinning of silicone rubber for faster curing.

The needle was mounted vertically above the collector plate. A special container which is called the "Charge modifier" was used to hold the solvent that surrounds the needle tip during the electrospinning as shown. The filled solvent helps to induce enough surface charges during the electrospinning, in case of silicone rubber. In addition, it keeps the electric field tangential to the fluid surface for solutions with high conductivity, above threshold.

The applied voltage and distance between the needle and collector were varied to execute proper electrospinning. SONY® DCR-HC28 camcorder was used to capture the image of jet formation from the Taylor cone during the electrospinning. Furthermore, the electrospun fibers were analyzed with an SEM model Leo 1530 Gemini.

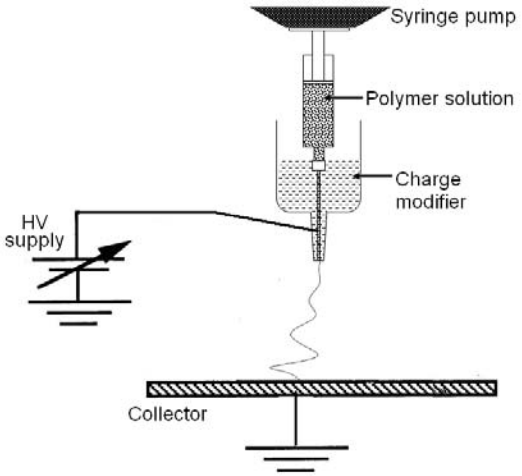


Fig.4: A schematic of the modified experimental setup used in the electrospinning process.

### *B. Material preparation*

Two different solutions were prepared to investigate the above modified electrospinning system. Sodium alginate (SA) with a viscosity of 0.25 Pas purchased from Aldrich® was chosen to prepare the solution with high conductivity. In addition, RTV615 silicon rubber manufactured by GE Silicones® was used to electrospin as it is a liquid at room temperature with high insulating properties. SA was electrospun using 3% and 4% (w/w) concentrations of SA in de-ionized water. Additionally, water was used as a solvent in the charge modifier for electrospinning of SA. Alternatively, RTV615 was prepared for electrospinning by mixing RTV615 part A and B in 10:1 ratio where RTV615 part B is a curing agent. Furthermore, ethanol was used in the charge modifier with RTV615. All solutions were stored at room temperature and all electrospinning experiments were done at room temperature and atmospheric air.

## IV. Results and Discussion

As illustrated in Fig. 5 (a), prior to the application of external electric field, the fluid droplet remains as it is, since there is no induced surface charges to form the Taylor cone and force a jet ejection. Fig. 5 (b) shows the behavior of a droplet of RTV615 silicone rubber during the electrospinning using a conventional electrospinning setup. It was difficult to observe ejection of any thin jet since there were not enough surface charges at the fluid surface. Since, RTV615 is a liquid with very low conductivity ($8.46 \times 10^{-10}$ S/m); it does not have the ability to transfer the induced ions in the fluid to the surface. However, as shown in Fig. 5 (c), with the use of a charge modifier, RTV615 could be electrospun because of the surrounding ethanol at the fluid surface, form enough surface charges to pull out a thin jet from the Taylor cone.

In the case of high conductivity solutions, as illustrated in Fig. 5 (d), prior to the application of an external electric field, SA droplet also remains at the tip of the needle without forming a Taylor cone. Similar to the behavior of RTV615, after the application of an external electric field with the conventional system, a jet of polymer solution was not

ejected from the SA droplet. As described in section II, the main reason for this behavior of SA is due to the significant decrease in tangential electric field at the fluid surface as a result of its high conductivity ($5.41 \times 10^{-1}$ S/m); hence, high recombination rate. However, the ejection of a thin jet from its Taylor cone could be achieved by using the charge modifier to release sufficient carriers to help form the Taylor cone. The differences in the jet shape with silicone rubber and SA could be related to the net charge at the surface of the cone, and the conductivity of the solution forming the cone.

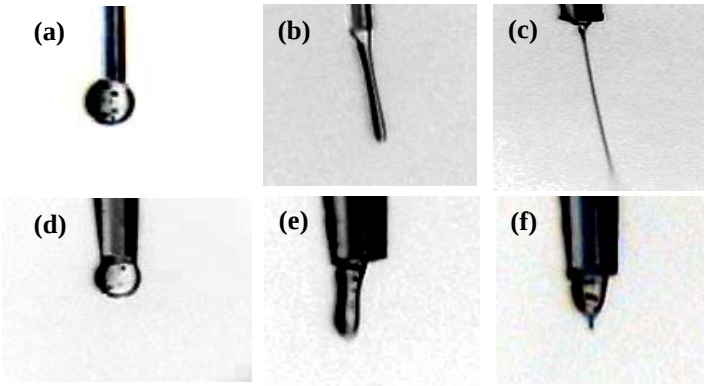


Fig.5: Electrospun jet behavior of different polymer solutions: (a) RTV615 without external electric field; (b) RTV615, using the conventional system; (c) RTV615, using the charge modifier and ethanol as a surrounding solvent; (d) SA without external electric field; (e) SA, using the conventional system; (f) SA, using the charge modifier and water as a surrounding solvent.

Eventhough, the Taylor cone and jet formation were observed with the use of charge modifier, SA and RTV615 produce nano and micro sized droplets during the electrospinning process, as opposed to long fibers. Fig. 6 shows the formed droplets of SA during the electrospinning process. The detailed results of electrospinning of RTV615 have been published in a companion paper [13]. The main cause that hinders the fiber formation of SA may be the lack of chain entanglements because of the rigid and extended SA chain conformations in the aqueous solution. Additionally, low molecular weight and reduced chain entanglements may restrict the fiber formation of RTV615.

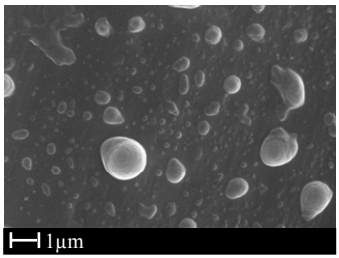


Fig. 6: An SEM image of electrospun SA droplets using water as a surrounding solvent.

On the other hand, zein/ethanol aqueous solutions are difficult to electrospin using the conventional electrospinning setup due to the rapid evaporation of the solvent at the sur-

face of the droplet. As a result, the droplet quickly dries and no jet or fiber formation is possible. However, the use of the proposed charge modifier with aqueous ethanol as a filled solvent can overcome this difficulty; thus, helps for continuous electrospinning of zein/ethanol aqueous solutions. The electrospun zein nanofibers are shown in Fig. 7. Uniform fibers of 200 to 300 nm in diameter were successfully spun.

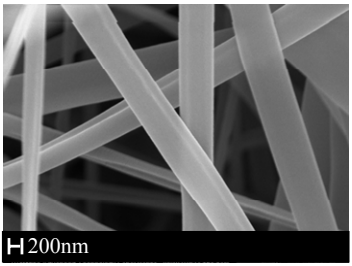


Fig. 7: An SEM image of electrospun zein fibers.

## ACKNOWLEDGEMENTS

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