Rheological Properties of Pullulan and Aloe Vera Nanofiber Solutions

Haifa El-sadi
Wentworth institute of technology
Boston, USA
E-mail: elsadih@wit.edu

Alex Bossart
Stevens institute of technology,
Hoboken, NJ

Sally Shady
Stevens institute of technology,
Hoboken, NJ
E-mail: sshady@stevens.edu

Dilhan Kalyon
Stevens institute of technology,
Hoboken, NJ

***Abstract*—Nanofibers have been used with increasing success for drug delivery and various biomedical engineering applications. The mixture of 13% pullulan-aloe vera can be pumped with a minor effects on the flow behavior. The fiber is then characterized by SEM, shear viscosity, storage and loss moduli. The oscillatory shear data is employed. The mixture has a complex rheological properties that includes extreme shear-thinning as well as viscoelastic properties and yield stress. The rheology of the pullulan- aloe vera nanofber was characterized, the measurement method may influence the results, it is unclear how the behavior near walls influence the measurement method, Parallel-plate rheometer is used to measure rheological properties. The data and rheological parameters should facilitate a better understanding of the process-ability characteristics of the mixture. The cross model provides a simple way of quantifying the viscosity/shear rate profile for a shear thinning mixture. SEM images are carried out.**

Keywords-Nanofiber; Rheology; Pulluan; Aloevera; Yield Stress

I. INTRODUCTION

Aloe vera is a therapeutic medicinal plant that has been used for many centuries to treat a wide range of ailments. There are over 250 species of the Aloe vera plant that have been studied. The most popular commercially grown are Aloe barbadensis miller and Aloe arborescens [1]. Many of the health benefits are associated with the structure and internal composition of the plant. Studies have shown that the active ingredients in the aloe vera plant have demonstrated wound healing, antifungal, anti-inflammatory, anticancer, immunomodulatory and gastroprotective properties [2-4].

Despite the exceptional healing properties of the aloe vera plant, there are several limitations with keeping these active ingredients stable. The bioactivity of the plant decreases approximately 6 hours after harvesting [1,5]. Exposure to light, humidity and temperature can also diminish these significant properties. Current techniques used to overcome these challenges have been focused on the usage of antioxidants and stabilizing agents. Such methods introduce other chemicals that would limit the scalability and purity of using non-toxic ingredients.

Pullulan is a linear polysaccharide produced by the polymorphic fungus Aureobasidium pullulans. Pullulan has a wide range of commercial and industrial applications in many fields such as food science, health care, pharmacy and even in lithography [6-8]. Pullulan is a water-soluble, low moisture permeable polysaccharide with excellent mechanical properties[9]. Due to these properties, pullulan is often used as a drug tablet coating. As a result, pullulan has been used in many drug delivery applications including nanotechnology [8, 10-12].

Nanofibers have been used with increasing success for drug delivery due to their extremely high surface to volume ratio, low density, and high porosity [reference]. In order to prevent aloe vera from degrading, it can be electrospun into nanofibers to encapsulate, preserve and administer the unique properties of aloe vera. Pullulan, is a biodegradable polymer with adhesive properties that can has been shown success in the electrospinning [10]. In this study, we investigate the rheological properties of pullulan-aloe vera nanofibers, which will provide insight into the material properties in a scaled-up manufacturing process.

II. MATERIALS AND METHOD

A. Nanofiber preparation

A mixture of polymer Pullulan Pf-20 food grade (Nagase, Japan), Molecular weight 200,000 g/ mol and fresh aloe vera were used to create nanofibers. To prepare the nanofibers, first aloe vera leaves were first washed and their outer green rinds were removed to obtain the gel fillet. The gel was then broken down by using a conventional blender (Ninja BL490T) at an agitator speed of 21000 rpm. The procedure was performed within 60s to avoid enzymatic decomposition [13]. A homogenous gel mixture was then formed using 13% pullulan. The solution was then electrospun using a Harvard apparatus PHD 4400 syringe pump at 28 and 30 kV with a distance of 20 cm and a flowrate of 7.2 µl/mine..

B. Scanning Electron Microscopy (SEM)

A Zeiss Auriga Focused ION FE SEM (Oberkochen, Germany). All materials were coated with gold nanoparticles for one minute using a Leica EM MED020 (Wetzlar, Germany) under vacuum. Analysis was carried out at 2.00 kV EHT, and estimation of the dimensions of the fibers was performed using ImageJ and DiameterJ.

C. Rheological Properties

Prepared mixture was loaded between two 50mm-diameter parallel plates with a gap of 0.5mm in rheometer (ARES). High frequency and strain were chosen to make sure that enough torque was generated for the transducer. Time sweep test with frequency of 50rps and strain of 10% was performed to analyze the evaporation effect of the mixture to the result. Prior to dynamic property measurements, strain sweep test at constant frequency of 50rps determined the linear viscoelastic regions. Frequency range of 1-100rps and strain of 10% (within linear viscoelastic region) was performed in frequency sweep test at room temperature to obtain dynamic properties (G’,G’’) of the mixtures. G’, the storage modulus which describes the elastic properties and G’’, the loss modulus, which describes the viscous properties, were calculated by a computer program of the rheometer by deconvolution the torque (shear stress) versus time data.

III. DISCUSSION

The homogenous solution of 13% pullulan in aloe vera were prepared to study the rheological properties of these nanofibers as shown in Figure 1. These properties will demonstrate the capabilities of the material solution in manufacturing processes such as 3D printing and extrusion. To our knowledge, this is the first study to prepare pullulan-aloe vera nanofibers from a fresh aloe vera plant. With the medicinal properties of aloe vera, pullulan is used as a carrier to help stabilize the bioactivity.

SEM images confirmed that pullulan- aloe vera nanofibers can be successfully developed as shown in Figure 2 and 3. The 28kV group produced 82 + 13 nm while the 30kV group was 99 + 21nm [10]. Fibers prepared at the 28kV setting produced nanofibers that were more consistent.

The storage (elastic) and loss (viscous) modulus of the mixture (pullulan and Aloe Vera) at 19oC for 3 s are increasing with the frequency as shown in Figure 4. The storage and loss modulus are almost constant at low frequency and increase significantly at higher frequencies which is related to the increase in the interaction between mixture components. It is observed that the viscous modulus is significantly larger than the storage modulus. It is very obvious that viscous modulus is higher than elastic modulus. Figure 5 shows the viscoelastic behavior of the mixture of pullulan and Aloe Vera, the complex modulus increases with increasing the frequency.

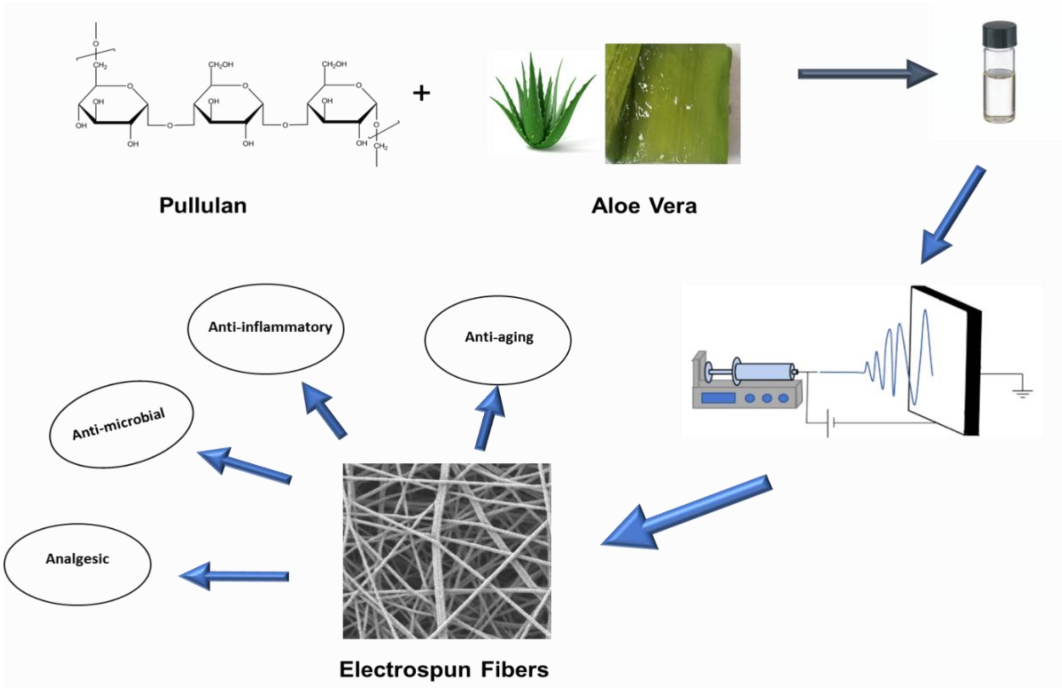

Figure 1. The overall process to develop the nanofiber demonstrating the multiple applications.

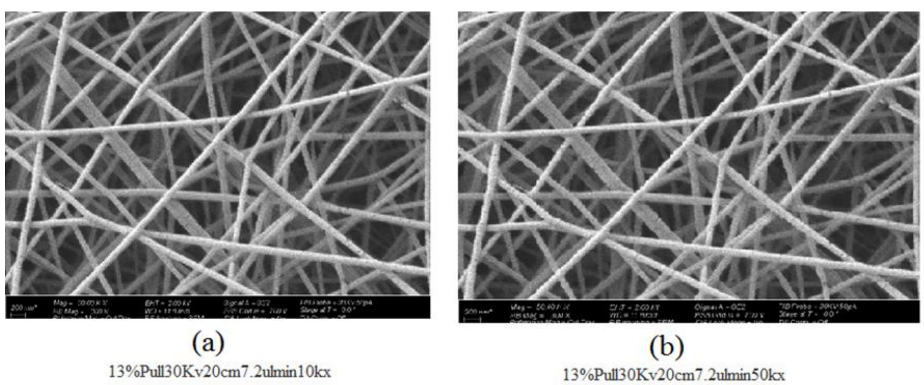

Figure 2. Nanofiber using PHD 4400 Syringe Pump at 30 kV (a) 10,000 times magnification, (b) 50,000 times magnification

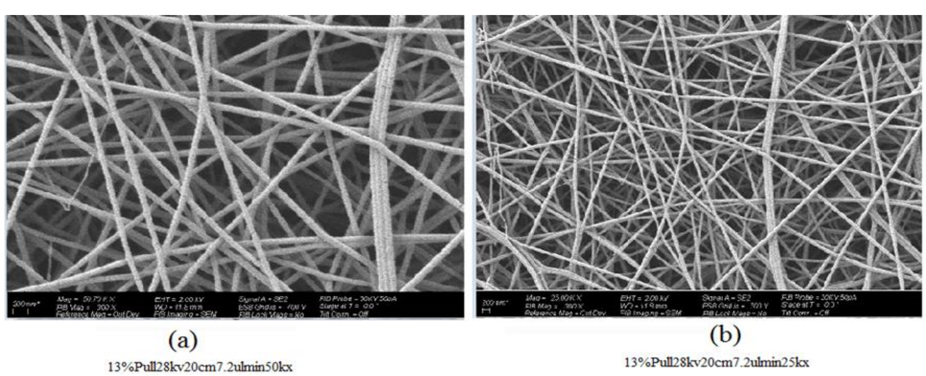

Figure 3. Nanofiber using PHD 4400 Syringe Pump at 28 kV (a) 50,000 times magnification, (b) 25,000 times magnification

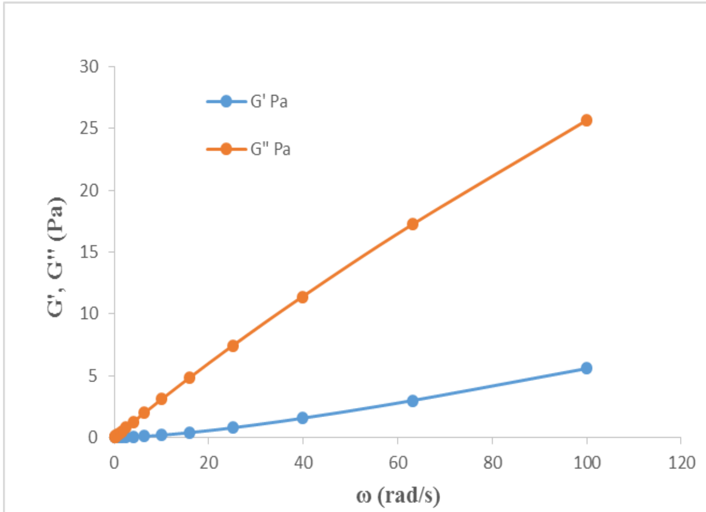

Figure 4. Elastic and viscous modulus of a mixture as a function of frequency at 19 oC.

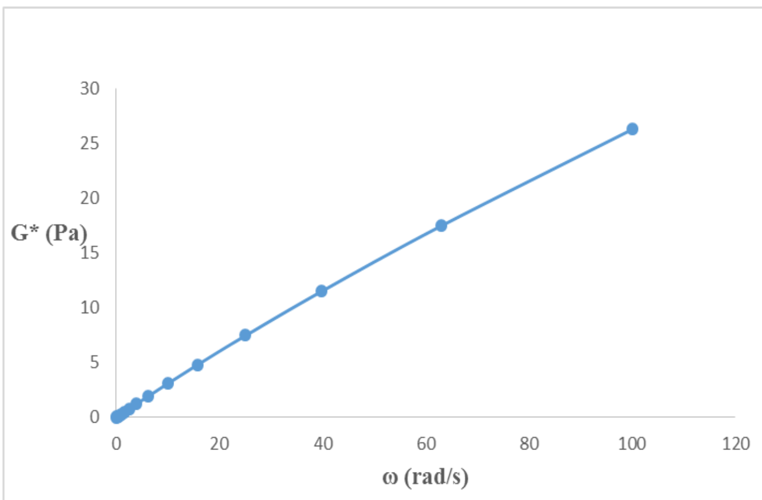

Figure 5. Complex modulus as a function of frequency at 19 oC

Figure 6 describes the changes in viscosity of the mixture of pullulan and aloe vera with respect to stress. The figure shows that the viscosity is decreasing with increasing the stress. Such viscosity decrease is directly related to the decrease of zeta potential. The yield stress is a key parameter in production, determining the force required to fill a product into its container or to flow. The stress at the viscosity maximum, is a measure for the yield stress. The yield stress is 0.07 pa which it shows that small amount of force is required to flow.

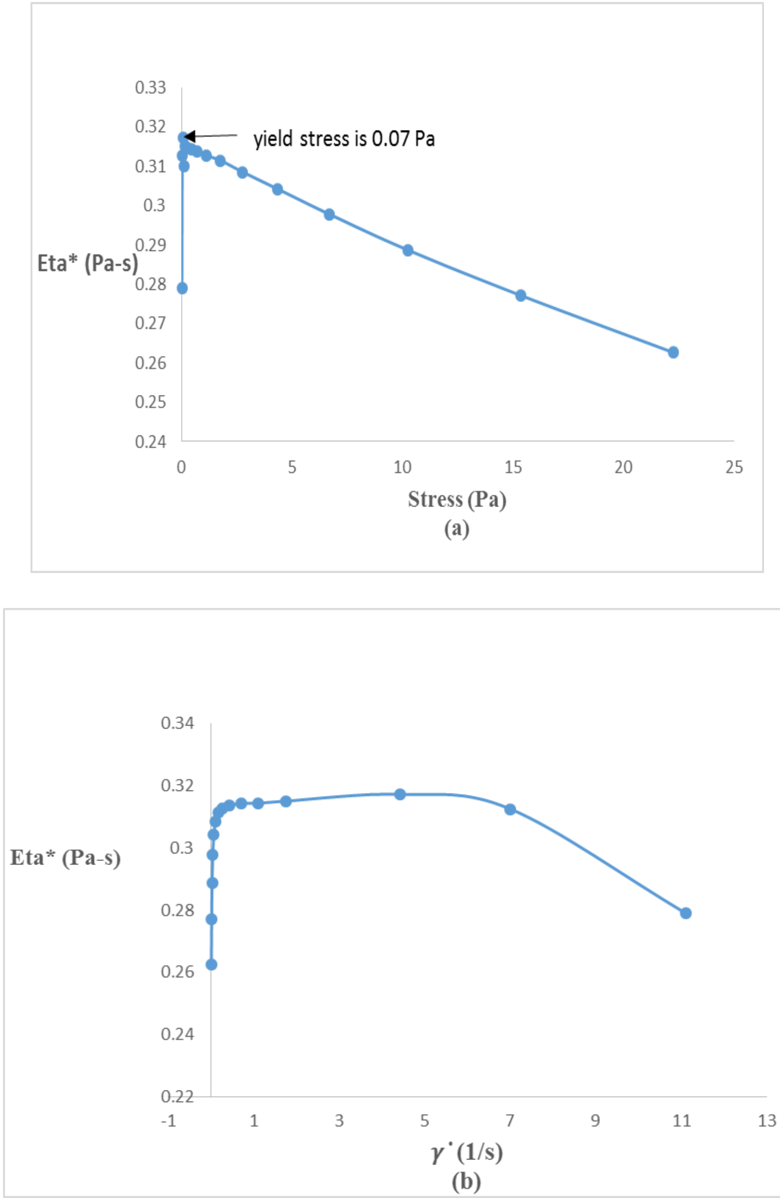

Figure 6. (a) Viscosity vs. stress, (b) Viscosity vs. shear rate

Cross rheological model shear thinning model gives a good agreement with measured data. $\dot{\gamma}$ is the shear rate, η_0, the zero shear viscosity and it is zero. m is the cross rate constant. It is dimensionless and is a measure of the degree of dependence of viscosity on shear rate in the shear thinning region. A value of zero for m shows Newtonian behavior and if m =1, it is due to increasing shear thinning behavior

$$\eta = \eta_\infty + \frac{\eta_{0-}\eta_\infty}{1+(c\dot{\gamma})^m} \quad (1)$$

$$\eta = \eta_\infty - \frac{\eta_\infty}{1+(c\dot{\gamma})^m} \quad (2)$$

C is the cross time constant and has time unit. m and 1/C are related to the texture of the mixture, pumping and the characteristics of mixing and pouring of the flow. Figure 7 indicates that at C=50, the cross model fits the experimental data at shear rate above than 1.76 1/s. this might be due to the experimental error. Above C=50 the cross model isn't applicable for this type of mixture.

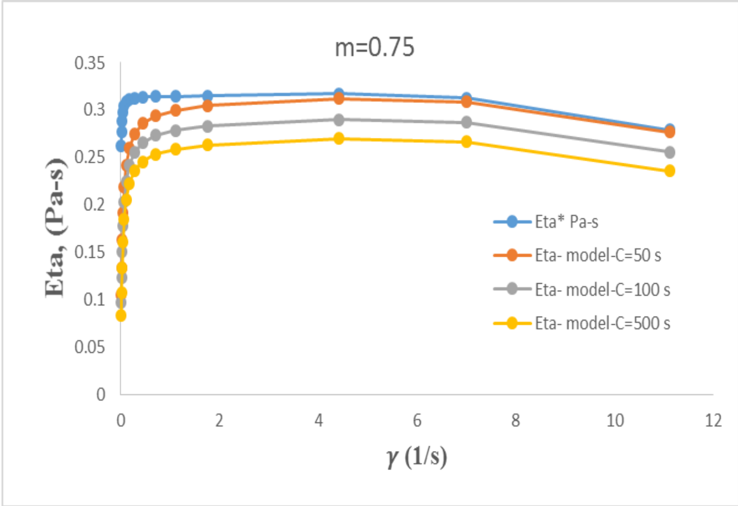

Figure 7. Validation of cross model with experimental data.

The rheometer was again used for stress relaxation experiments. The mixture of pullulan and Aloe vera is stable under temperature 19 oC as shown in Figure 8. However viscous modulus is higher than elastic modulus of the mixture.

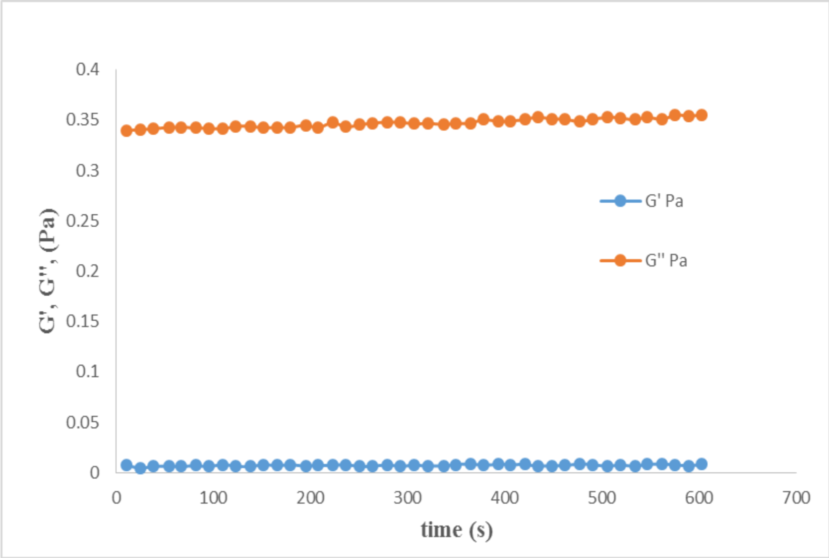

Figure 8. Storage and loss modulus vs. time

IV. Conclusion

The objective of this research is to study the flow behavior of the mixture of pullulan and aloe vera. Different samples of the mixture have been carried out. It is concluded that the mixture of 13% pullulan-aloe vera can be pumped with a minor effects on the flow behavior. The rheological properties of nanofiber at 50,000 times magnification using PHD 4400 Syringe Pump at 28 kV with a distance 20 cm were carried out. The yield stress is small since it is a key parameter in production, the mixture requires small force to flow. The viscosity decreases with increasing the shear rate. The cross model gives a good agreement with measured data at cross time constant 50 s. However, elastic modulus doesn't change with increasing the frequency. In the future, more rheological tests will be studied to indicate better predications of the fluids behavior.

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