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MECHANICAL AND MORPHOLOGICAL PROPERTIES OF SOLUABLE STARCH BASED NANOFIBERS

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Abstract: *Starch is one of the most important renewable and environmentally friendly source in sustainable societies, in addition to its remarkable potential to manufacture nanofiber through electrospinning method. This method is an inexpensive and simple process for the fabrication of micro- and nano-scale fibers. The current study refers that soluable starch (SS)/Poly (vinyl alcohol) (PVA) nanomats were fabricated in the same process parameter values that flow rate, voltage and distance using electrospinning method.*
In this study, processability, tensile strength and morphology of five different mass ratios (10:90, 15:85, 20:80, 25:75, 30:70) of SS/PVA solution were investigated. Also, viscosity, conductivity values and fiber diameters of samples were compared according to starch content in solution. Surface morphologies of nanofibers were determined by Field emission scanning electron microscope (FE-SEM) and mechanical properties of the resultant products were characterized by Universal test machine.
The results showed that uniform and bead-free nanofibers were produced at the sample 2 (15:85) mass ratio of SS/PVA. A better vertical mechanical strength was obtained at sample 2 (15:85) mass ratio as compared with other samples. On the other hand, sample 3 (20:80) had the slighly highest horizontal mechanical strength than sample 2. The average diameters of electrospun samples ranged from 79.6 to 136nm.

Key words: *electrospinning, starch, PVA, tensile strength, morphology*

1. INTRODUCTION

Electrospinning which an inexpensive and simple synthesis method for one-dimensional (1D) nanostructures such as nanofibers.

Starch which is a polysaccharide [1] is widely obtained from many natural sources i.e. cassava, corn, potatoes, and wheat. It has many advantages as its nontoxicity, biodegradability [2][3] and long-term durability so that it uses as a filler to strengthen plastics or as a matrix to develop composite structure. Besides its advantages, starch offer many disadvantages including water sensitivity, brittleness, and poor mechanical properties [4].

Poly (vinyl alcohol) (PVA) is an electrospinable, biodegradable [5], biocompatible, nontoxic and synthetic water soluble polymer[6] that is generally used for biomedical applications in tissue engineering and wound dressing [7][8][9][10][11].

In the present study, nanofibers that are the blends of PVA and soluable starch (SS) in the different mass ratios (SS:PVA; 10:90, 15:85, 20:80, 25:75, 30:70) fabricated using same

electrospinning process parameters such as voltage, flow rate and distance. Solution characterization tests that are viscosity and electrical conductivity were performed. Then, morphological and mechanical strength studies of nanomats carried out.

2. MATERIALS AND METHODS

2.1. Material

Nanofiber solution was prepared with PVA polymer granules and soluable starch. Poly (vinyl alcohol) (PVA) was purchased with molecular weight of 70.000 g/mol. Soluable starch was dissolved in Dimethyl sulfoxide (DMSO) (purity ≥ 99.9 %) . All these ingredients were supplied by Merck firm.

2.2. Methods

Firstly, PVA solution 12% (w/v) was prepared by dissolving of PVA polymer granules in distilled water at 80℃ under constant stirring for 2 hr. Following that, %10 w/v starch was dissolved in (DMSO) at 100°C for 1 hour. Lastly, the prepared solutions were mixed in different mass ratio such as 10:90, 15:85, 20:80, 25:75 and 30:70 (Starch:PVA) in Table 1.

Electrospinning was performed in Inovenso, NE300 Nanospinner laboratory type machine at room temperature using a cylindrical collector covered with oily paper. The five prepared solutions were fed to a 10 ml plastic syringe which connected to a stainless steel needle for electrospinning. The electrospinning parameters such as feed rate, voltage and needle to collector distance were fixed as 0.4 ml/h, 25 kV, and 13 cm respectively. Total production time for each sample adjusted as three hours.

Table 1: *Process parameters of solution*

Sample No	Starch/PVA	Flow (ml/h)	Voltage (kV)	Distance(cm)	Time (h)
1	10: 90	0,4	25	13	3
2	15: 85	0,4	25	13	3
3	20: 80	0,4	25	13	3
4	25: 75	0,4	25	13	3
5	30: 70	0,4	25	13	3

The viscosity of the solutions was determined by using viscometer (Brookfield DV-E Viscometer, USA) at room temperature. The viscosity measurement was performed with S21 spindle at 100rpm. The electrical conductivity values of the solutions were measured by conductivity meter (WTW Cond 3110, Germany) at room temperature.

Morphological characterization of the electrospun nanofibers were done using Field Emission Scanning Electron Microscopy (FEI SIRION XL30 FEG). The mechanical properties (Tensile strength and elongation at break) of electrospun nanomats in the horizontal and vertical directions were tested with Instron 4411 Universal Test using 30 mm/min stretching speed.

Nanomats were cut into rectangular pieces as 50 x 10 mm (length x width) at room temperature. Five different samples were used to analyze each sample.

3. RESULTS AND DISCUSSION

The nanofiber structure and properties are influenced by the viscosity of polymer solution [12]. It is reported in the literature that increase in starch concentration resulted an increase in viscosity and conductivity [1]. But in this study, viscosity and conductivity decrease with increasing amount of SS shown in Figure 1. The reason for this is thought to be caused by SS (soluable) rather than starch. Liu and others reported that the increase in starch ratio decreases viscosity and nanofiber diameter by using soluable starch [13].

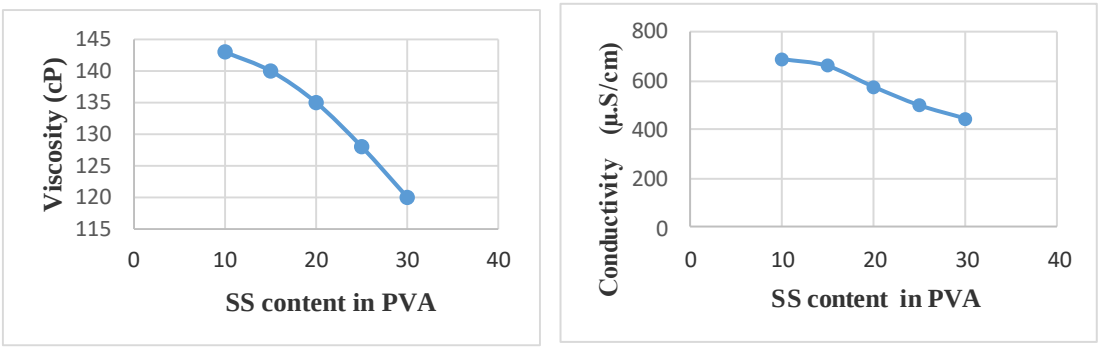

***Fig. 1**: The viscosity and conductivity of the polymer solution with the changes of SS ratios in PVA*

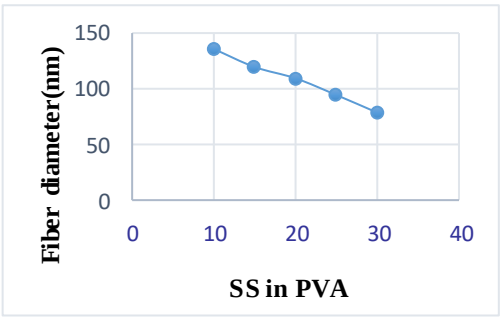

***Fig.2**: Average fiber diameter of samples with the changes of SS ratios in PVA*

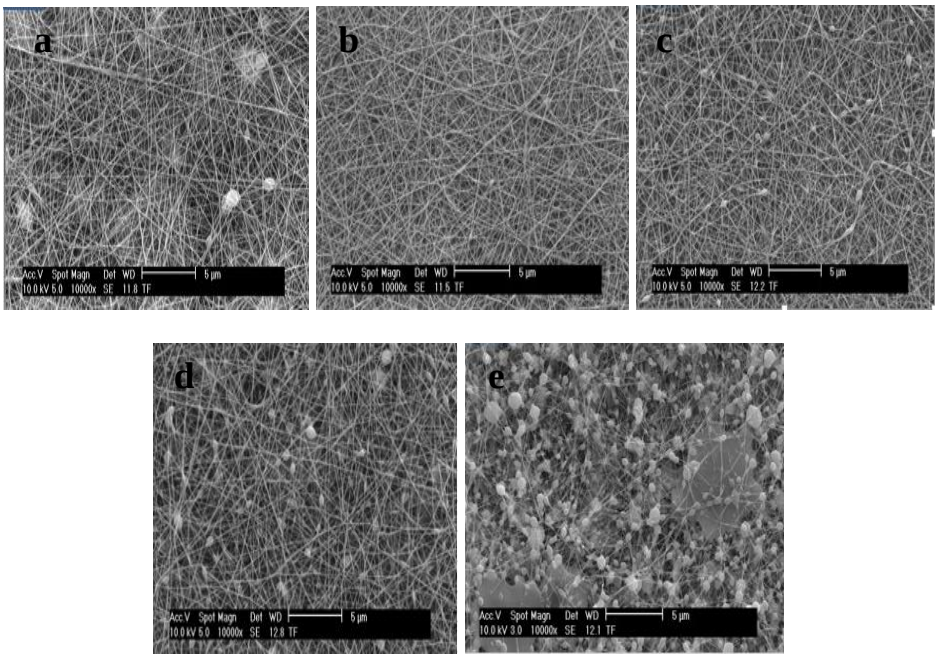

***Fig 3**: Scanning electron microscope images of the nanofibers at x10.000 of magnification*

a)10:90, b)15:85, c)20:80, d)25:75, e)30:70

The SEM image of SS/PVA nanofibers with various SS ratio are given in Figure 3. Scanning electron microscope images of sample 2 (15:85) (Figure 3 (b)) indicate that the nanofibers are smooth, bead-free, and randomly oriented. However, as seen in Figure 2 sample 1 (10:90) has shown slightly better results than sample 2 (15:85). On the other hand, the high ratio of soluable starch sample 5 (30:70) exhibits too much beads, and nonuniform nanofibers because of low viscosity, conductivity and fiber diameter.

The fibers diameter which was calculated on the SEM image by using the Image J illustrated in Figure 2. The highest fiber diameter (136 ± 10 nm) belong to sample 1 (10:90). The thinner fibers belong to sample 5 (30:70). The average fiber diameter decreases from 136 to 79,6. In this study, it was observed that the decrease in viscosity decreases the produced nanofiber diameter. And, as the conductivity of the solution decreased, the nanofiber diameter decreased.

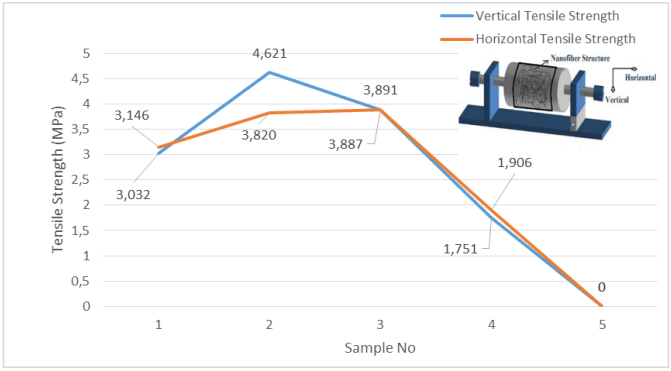

***Fig 4:** Mechanical properties and vertical-horizontal directions of samples*

The mechanical properties of SS/PVA samples are given in Figure 4. It was showed that the highest vertical tensile strength was obtained for sample-2 (15:85 SS/PVA), followed by sample 3 (20:80 SS/PVA), sample 1 (10:90 SS/PVA) and lastly sample 4 (25:75 SS/PVA). It was indicated that the highest horizontal tensile strengths was acquired respectively sample 3, sample 2, sample 1 and sample 4. Mechanical strength of sample 5 cannot be measured the reason of a very brittle structure. The reduction in average fiber diameter leads to this dramatic decrease of the tensile strength. The mechanical strength decreased generally as the amount of SS increased.

4. CONCLUSIONS

SS nanofibres were fabricated successfully by blending with PVA to enhance the spinnability of the starch using electrospinning technique. Measurements showed that the mass-varying proportions of SS in solution had a significant effect on solution properties (viscosity and conductivity), fiber diameter, morphology and tensile strength. An increase of SS proportion in solution is able to reduce nanofiber diameter. Uniform bead free SS/PVA nanofibers were obtained at the concentration of SS (10 w/v %) and PVA (12 w/v %) in the mass ratio of 15:85. Sample 5 (30:70) is fragile and does not have enough strength because of very few nanofibers and so many beads. Sample 2 (15:85) has the best total strength due to non-bead and uniform structure of nanomat. A higher ratio of SS in sample 5 (30:70) resulted non-uniform and more beaded structure, and lower mechanical strength of nanofibers than the rest of sample.

So far, many researches have been conducted on nanofibers and electrospinning; still, more controllable, more cost effective, more environmentally friendly and safer methods are of essential importance to future applications of nanofibers [14]; therefore with this current study we believe that future studies will be high interest of biodegradable nanofibres i.e. SS starch films.

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