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Research Article**Effect of polymer and surfactant concentrations on PVP nanofibers morphology****Hülya Kesici Güler^a  and Funda Cengiz Çallıoğlu^{a,*} **^a*Süleyman Demirel University, Engineering Faculty, Textile Engineering Department, Isparta, Turkey*

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ABSTRACT

In this study, biocompatible polyvinylpyrrolidone (PVP) based nanofiber production was carried out with various polymer and surfactant concentrations. Firstly; various concentrations of PVP (6, 8, 10, 12, 14, 16 wt %) polymer solutions were prepared, solution properties (conductivity, viscosity, surface tension, pH and density) were determined and nanofiber production was achieved under the optimum process parameters. 12 wt % PVP concentration was chosen as an optimum in terms of nanofiber morphology and fiber fineness. Then, polymer concentration was kept constant at 12 wt % and various concentrations of surfactant (1, 2, 3, 4, 5, 6 wt %) added into the polymer solutions. According to the solution properties and Scanning Electron Microscope (SEM) images; conductivity, viscosity and average fiber diameter increased with polymer and surfactant concentrations increase and ultra-fine, bead free and uniform nanofibers were obtained. On the other hand, surface tension and pH values were affected by polymer concentration changing, however, surface tension decreased significantly and pH decreased slightly with the addition of surfactant to the PVP polymer solution. Moreover, the density of polymer solutions increased with both polymer solution and surfactant concentration increase.

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1. Introduction

Electrospinning is a dry spinning process that technic to produce nanoscale fibers. It is widely using to produce polymeric nanofibers. Advantages of this technic, most polymers can be used for nanofiber production and easy to set up this apparatus [1-2]. Nanofibers have unique properties than compared conventional fibers such as; small fiber diameter (nm), high porosity and large specific surface area (m²/g) [3].

PVP is a polymer that is biocompatible, hydrophilic, synthetic, non-toxic, dissolve in water and many other solvents. Because of these properties, it can be used for medical and cosmetic application areas such as; drug delivery and release, tissue engineering, wound dressing [4-5]. Polymer concentration and surface tension are important factors for spinnability and smooth (bead free) fiber production. Therefore, in literature, there are many studies about this subject [6-11]. Surfactants usually used to reduce the surface tension of polymer solutions for the overcome of electrostatic forces in the electric field [12].

Surfactants can be defined as a stick that has two different parts one of them is a hydrophilic head and another one is a hydrophobic end. Generally, surfactants work that hydrophobic part sticks to the organic phase and hydrophilic head part hold on to the water [13]. In this study, Cremophor RH 40 was used as a nonionic surfactant. Cremophor RH 40 which is a non-toxic commercial surfactant can be used in medical and cosmetic application areas [14]. Surfactants such as Triton X-100, Hexadecyltrimethylammonium Bromide (HTAB), Tween80, sodium dodecyl sulfonate (SDS), cationic cetyltrimethyl ammonium bromide (CTAB), Efska3030 have been used to make a positive impact on the morphology of nanofibers and reduce surface tension of polymer solutions [15-17]

On the other hand, in literature there are some studies effect of polymer concentration on nanofiber morphology such as poly(ethyleneoxide) (PEO) [6], polyvinyl butyral (PVB) [7], poly(vinylidene fluoride) (PBDF) [8], cellulose acetate and poly (vinyl chloride) [9], poly(ethylene terephthalate) (PET) [11].

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The aim of this study is the investigation of the effect of polymer and surfactant concentrations on PVP nanofiber morphology. In addition, this study contributes to the PVP nanofibers morphology with details.

2. Experimental Study

2.1 Material

In this study, PVP K30 (Mw 360.000 g/mol) was used as a polymer, distilled water was used as a solvent and Cremophor RH 40 was used as a surfactant. PVP was purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA) and Cremophor RH 40 was supplied from Ersa Chemistry (İzmir, Turkey).

First part of this study; PVP/distilled water polymer solutions with various polymer concentrations optimization was carried out to obtain fine and bead-free nanofibers. For this purpose, polymer solutions were prepared at six different PVP concentrations. The solution contents and sample codes are given in Table 1.

PVP polymer solution concentration was kept constant at 12 wt % for the second part of the study and various concentrations of surfactant was added into the polymer solutions. The solution contents with various surfactant concentrations and sample codes are given in Table 2.

All solutions were prepared under the same conditions such as; stirring time, stirring speed and temperature.

2.2 Methods

Polymer solutions were characterized after all solutions were prepared. Conductivity was measured with Selecta CD 2005 conductometer, viscosity values were obtained from Lamy Rheology, B-One Touch Screen under a shear rate of 5 s^{-1} , surface tension and density were determined with Biolin Scientific Sigma 702 by Wilhelmy plate method and pH was evaluated using Adwa AD110.

Nanofiber production was achieved via the electrospinning method under the optimum process parameters (voltage, distance between electrodes, solution feed rate). These process parameters are given in Table 3.

To characterize fiber morphology of PVP based nanofibrous surfaces, SEM images were taken at 1.000 times and 20.000 times of magnifications.

Table 1. Various concentrations of PVP polymer solutions and sample codes

Sample Codes	Polymer Concentration (%)
PVP6	6
PVP8	8
PVP10	10
PVP12	12
PVP14	14
PVP16	16

Table 2. Sample codes of PVP polymer solutions with various concentrations of surfactant

Sample Codes	Polymer Concentrations (%)	Surfactant Concentrations (%)
PVP12-1	12	1
PVP12-2	12	2
PVP12-3	12	3
PVP12-4	12	4
PVP12-5	12	5
PVP12-6	12	6

100 different measurements were obtained from each nanofiber samples to determine average fiber diameter with ImageJ software. The statistical analysis program was used for drawing histogram curves. Besides, the fiber uniformity coefficient was calculated from the ratio of A_w/A_n and optimum value is close to 1, which represents uniform fibers. Number average and weight average values were calculated using formulas (1) and (2), given below [18].

$$A_n = \frac{\sum n_i d_i}{\sum n_i} \text{ (number average)} \quad (1)$$

$$A_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \text{ (weight average)} \quad (2)$$

3. Results and Discussion

Various concentrations of PVP solutions properties such as conductivity, viscosity, surface tension, density and pH were determined. Conductivity, viscosity and surface tension graphs for various concentrations of PVP solutions are given in Figure 1.

According to the Figure 1 (a), viscosity and conductivity increases with polymer concentration increase. Solution viscosity increase with polymer concentration is expected result as known from the literature [19]. Because polymer entanglement increases with polymer concentration which causes higher viscosity. Conductivity is related to the number of ions in the polymer solution [20]. According to the conductivity results; it is thought that the number of ions increases with PVP polymer concentrations. Surface tension was not affected by PVP concentration increase (Figure 1 (b)).

Viscosity, conductivity and surface tension graphs for PVP (12 wt %) solutions with various concentrations of surfactants are given in Figure 2.

As it has seen in Figure 2 (a); viscosity and conductivity increase with surfactant concentration increase. This result is compatible with the literature [21]. There is also a strong relationship between the surfactant and surface tension of the solution. It has been seen clearly in Figure 2 (b), the addition of surfactant to the PVP polymer solution (1w% surfactant) decreased surface tension significantly.

All solution properties determined from this study are given in Table 4.

Table 3. Process parameters of electrospinning

Voltage (kV)	Distance between electrodes (cm)	Solution feed rate (mL/h)	Humidity (%)	Temperature (°C)	Spinning Duration (min)
26.4	16.5	0.6	35	21	30

Table 4. Solutions properties for all samples

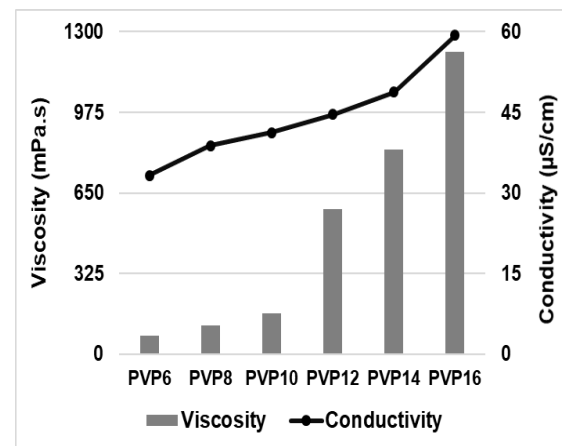
Sample Codes	Conductivity ($\mu\text{S}/\text{cm}$)	Viscosity (mPa.s)	Surface Tension $\pm\text{SD}^*$ (mN/m)	Density (kg/L)	pH
PVP6	33.3	76	59.00 \pm 0.21	1.0046	5.89
PVP8	38.8	115	63.49 \pm 0.44	1.0129	5.54
PVP10	41.2	164	59.61 \pm 0.91	1.0158	5.44
PVP12	44.6	583	63.02 \pm 1.15	1.0218	5.47
PVP14	48.8	826	52.29 \pm 1.97	1.0289	5.38
PVP16	59.3	1218	49.89 \pm 2.14	1.0426	5.38
PVP12-1	56.9	585	42.41 \pm 2.40	1.0224	5.07
PVP12-2	66.3	969	41.29 \pm 2.08	1.0241	4.93
PVP12-3	74.8	1102	40.00 \pm 2.26	1.0333	4.86
PVP12-4	85.3	1267	39.28 \pm 1.55	1.0434	4.80
PVP12-5	89.3	1551	39.27 \pm 2.04	1.0597	4.73
PVP12-6	98.8	1920	38.89 \pm 1.93	1.0730	4.73

*SD: Standard Deviation

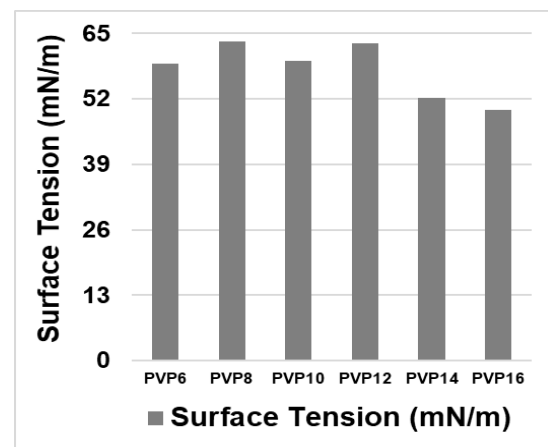
According to Table 4; it is possible to say, there is no relation between polymer concentration and surface tension however, surfactant concentration influences the surface tension of polymer solution noticeably. Besides, density increases slightly with polymer and surfactant concentrations. And, it was determined that the addition of surfactant was decreased pH slightly also.

SEM images and fiber diameter histogram curves for various concentrations of PVP solutions are given in Figure A.1 (in Appendix). And also, relationships between average fiber diameter and fiber diameter uniformity coefficient are given in Figure 3.

As it has been shown clearly in Figure A.1, beads formation can be seen intensively on the nanofibrous structure from PVP polymer solutions with 6 and 8 wt % concentrations. For this reason, fiber diameter could not be measured and histograms could not be drawn. It is determined that beads formation decreases with polymer concentration increasement and all beads were disappeared at 16 wt % PVP polymer concentration. When histograms were analyzed, the average fiber diameter increases with polymer concentration increasement. In Figure 3, it is seen that uniformity increases with PVP concentration in other words fiber diameter uniformity coefficient approaches to value of 1. It is possible to deduce from these results; there is a relationship between solution viscosity and nanofiber morphology. Viscosity is related to polymer molecule chains entanglement in the solution. Lower viscosity causes lower molecule chain entanglement therefore, electrospinning and beads may occur. On the other hand, smooth and bead-free nanofibers can be produced at higher viscosity [13].

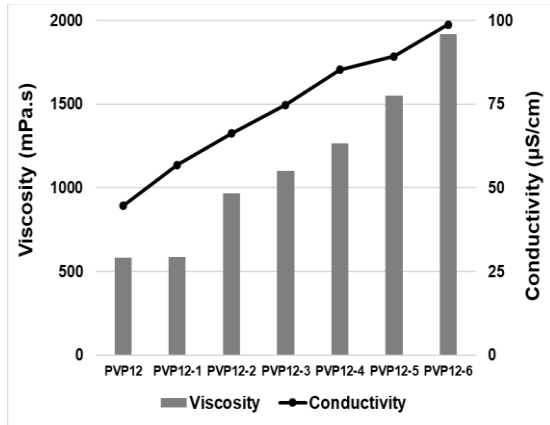


(a)

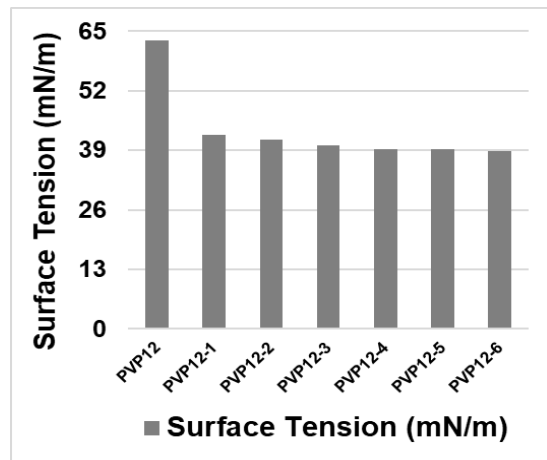


(b)

Figure 1. Conductivity, viscosity, and surface tension results of PVP solutions



(a)



(b)

Figure 2. Conductivity, viscosity and surface tension results of PVP solutions with various surfactant concentrations.

In the literature, it is clearly seen in the studies of PVP nanofibers that the average fiber diameter increases as the polymer concentration increase [22-24].

SEM images and fiber diameter histogram curves of PVP nanofibers with various concentrations of surfactants are given in Figure A.2 (in Appendix). The relationship between average fiber diameter and fiber diameter uniformity coefficient is also given in Figure 4.

According to Figure A.2. and Figure 4; it is possible to say, fiber morphology has improved, the beaded structure has been removed and the average fiber diameter has increased slightly with surfactant concentration increase. Generally, ultra-fine (approx. 200-250 nm) and uniform nanofibers were produced. It is well known from the literature; beads can be minimized with lower surface tension of the polymer solution. Elimination of beads can be realized in two different ways. One of them is of using surfactant and the other one is the selection of solvent which has low surface tension [25]. In this study, using of a surfactant was preferred to minimize the number of beads into the nanofiber structure. There are similar studies in the literature on non-ionic surfactants, both beads decreased and average fiber diameter increased [16, 26-27].

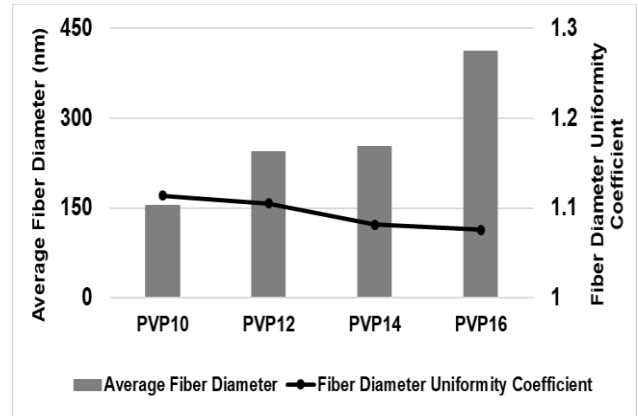


Figure 3. Average fiber diameter and fiber diameter uniformity coefficient of PVP nanofibers

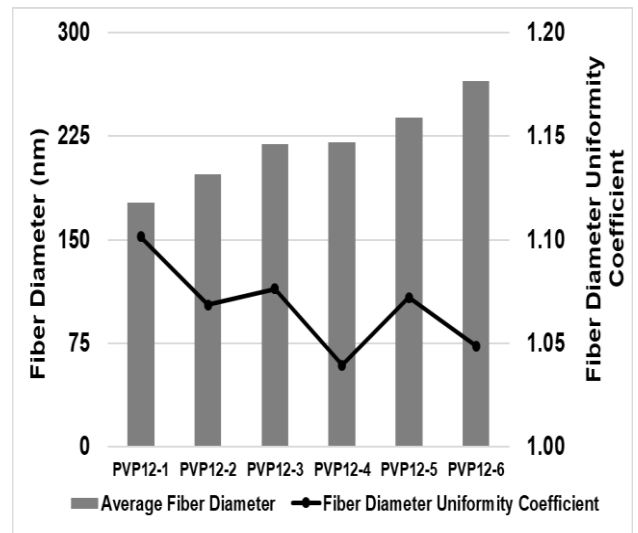


Figure 6. Average fiber diameter and fiber diameter uniformity coefficient of PVP nanofibers with various concentrations of surfactant

4. Conclusion

Within the scope of the study, biocompatible PVP based nanofibers with various polymer and surfactant concentrations were produced by the electrospinning method.

Optimum polymer concentration was determined as 12 wt % PVP in terms of fiber morphology and fiber diameter. Various concentrations of surfactants such as 1, 2, 3, 4, 5, 6 wt % were applied to the PVP solution at 12 wt % polymer concentration. Generally; viscosity, conductivity and average fiber diameter increase with polymer and surfactant concentration increase and beaded structure was eliminated. Surfactant addition has been affected solution surface tension while polymer concentration has not. Moreover, density was increased both polymer and surfactant concentrations. According to the results; ultra-fine, smooth and uniform fibers have been produced, and these biocompatible nanofiber materials are thought to have potential in the medical and cosmetic industry.

Declaration

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article. The author(s) also declared that this article is original, was prepared in accordance with international publication and research ethics, and ethical committee permission or any special permission is not required.

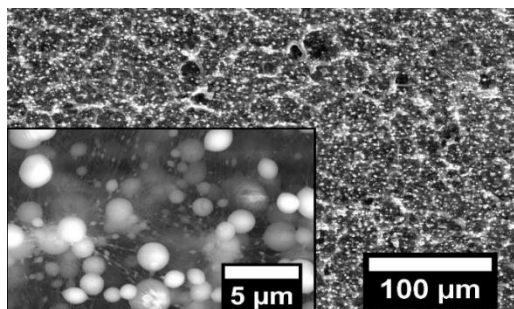
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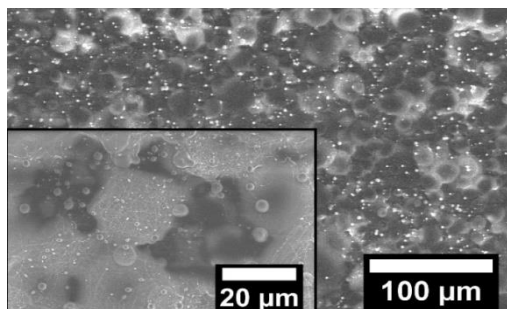
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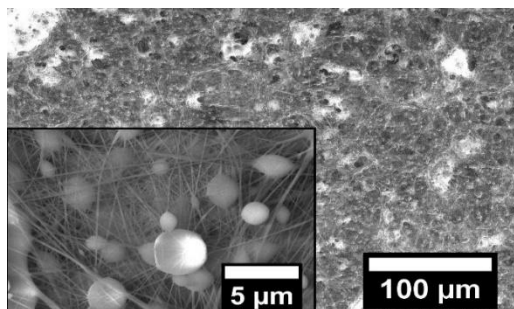
Appendix



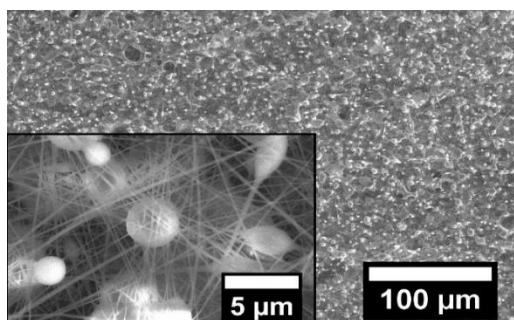
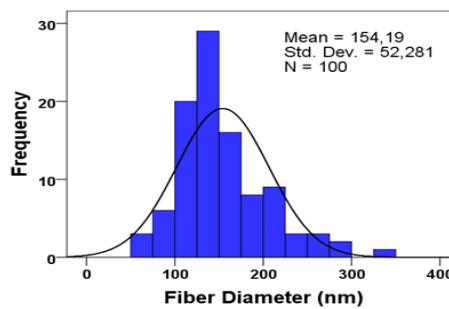
PVP6



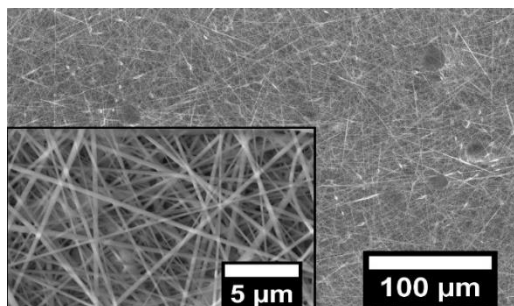
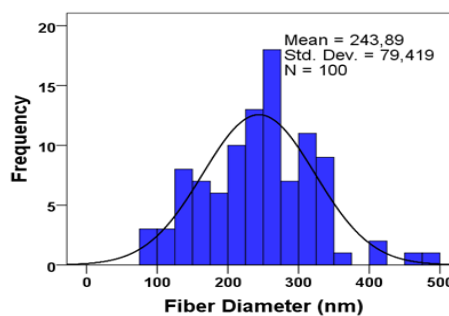
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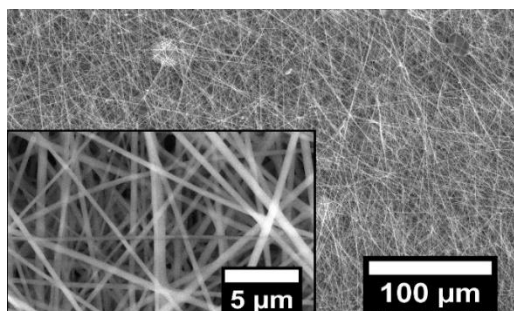
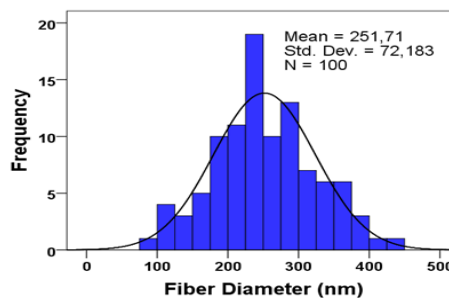
PVP10



PVP12



PVP14



PVP16

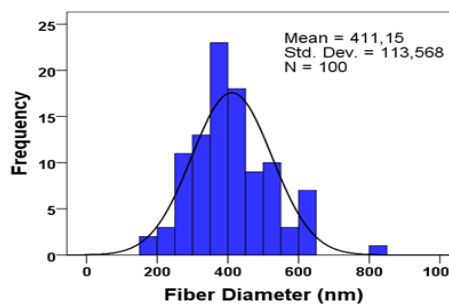
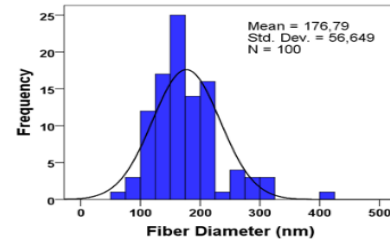
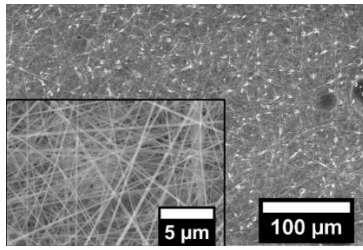
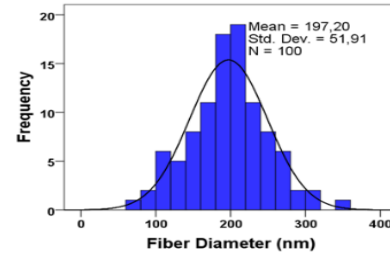
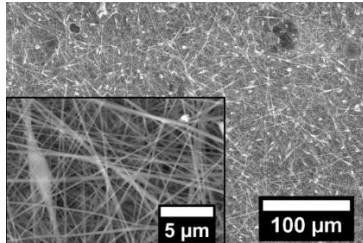


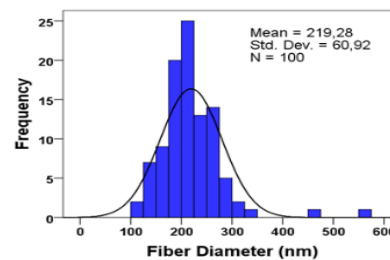
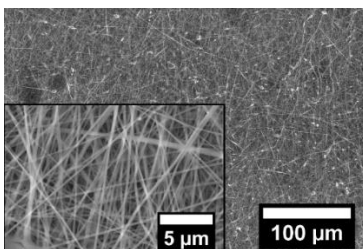
Figure A.1. SEM images (1.000x and 20.000x) and histograms of PVP nanofibers



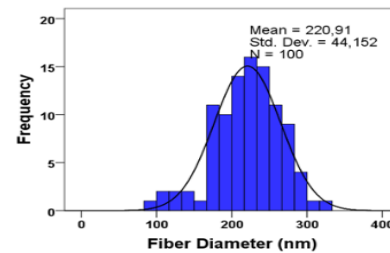
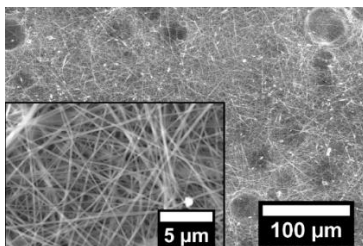
PVP12-1



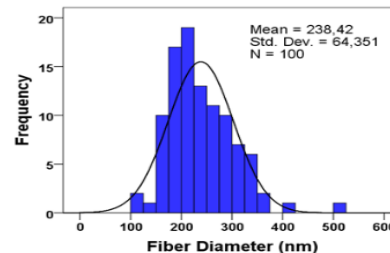
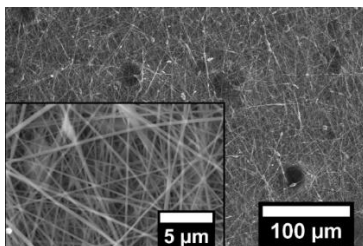
PVP12-2



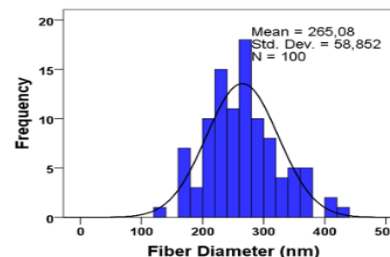
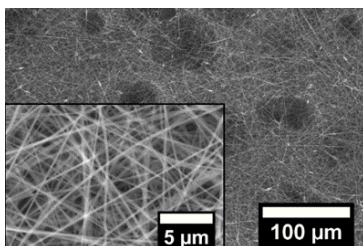
PVP12-3



PVP12-4



PVP12-5



PVP12-6

Figure A.2. SEM images (1.000x and 20.000x) and histograms of various surfactant concentrations of PVP nanofibers