

# Effect of Silver Nanoparticles on the Morphology and Structural Properties of Poly (Vinyl Pyrrolidone) Polymer Nanofibers Prepared by Electrospinning Method

Abeer Khudhair Atya\*<sup>1</sup> Sahib Neamah Abdul Wahid<sup>1</sup> S M.Thahab<sup>2</sup>

<sup>1</sup>Department of Physic, Faculty of Education for Girls, University of Kufa, Najaf, Iraq

<sup>2</sup>Department of Physic, Faculty of Science, University of Kufa, Najaf, Iraq.

## Abstract

In this research the morphology and structural properties of Poly (vinyl pyrrolidone) (PVP) polymer nanofibers with the addition silver nanoparticles have been studied and investigated. It was observed that the pure Poly (vinyl pyrrolidone) (PVP) nanofibers and PVP nanofiber doped by silver nanoparticles (AgNPs) which have a diameter ranging (34 to72) nm and (81 to98) nm respectively. Longer length of PVP fiber was obtained with the PVP fiber length. The morphology of AgNPs and doped PVP nanofibers were analysis using scanning electron microscope (SEM). The SEM results show that the AgNPs has a spherical shape which is agreed with Atomic Force microscope (AFM) results. It was observed that the PVP which dissolved in ethanol can be produced smooth nanofiber because of low surface tension. Energy Dispersive X-ray Spectrometry (EDS) analysis shows the percentage of the AgNPs elements of the PVP/AgNPs nanofibers samples

**Keywords:** Electrospinning, PVP, Nanofiber, AgNPs, SEM

## INTRODUCTION

Electrospinning process is extensively used to create fiber with nanoscale or submicron diameter. The subsequent fibers have single properties, for example large surface area to size ratio, high porosity, lesser pore volume [1,2] furthermore, the electrospinning method provides important compromise, considering quantity and the control of the shape and volume that The electrospinning process and morphology of nanofibers influenced by four kinds of parameters polymer solution parameter including (surface tension, concentration, electrical conductivity and viscosity), structural properties including (molecular weight), processing conditions including (spinning distance, nozzle geometry, feed rate and voltage) and ambient parameters including (atmosphere pressure, relative humidity and temperature) [5] fiber diameter of electrospun fiber decreasing with increasing the distance amid the polarity. Also in case decreasing distance the fiber are not totally stabilized and finally the cross units of spinning fiber convert to flatter. The fibers showed a straight, cylindrical morphology representing that the fibers are typically dried when the fall on the collector. Where the polymer solution have properties for example rheological properties of polymer solution, particularly solution viscosity and electrical conductivity, effect the fiber creation morphologies as well as diameter of electrospinning method, also boiling points of the solvent which used in the study effect on fiber diameter such as ethanol is 153C° where the solvent has lower boiling points undergo to the faster evaporations after the splitting and spraying of an unbalanced jet [6] nanofibers and nanotubes created from polymers offer wide range of uses in areas such as sensors photonics, filtration, medicine and catalysis. Via utilizing nanofibers to create bulk materials [7].

One application of nanofibers existence used is fabrication of filtration media. As electrospun nanofiber further filters are suitable for eliminating particles in submicron ranges. As the small particles of fewer than 0.5 micrometer which can be easily trapped in the electrospun nanofibrous inside filters because of its tall surface area to size ratio and tall surface cohesion and so improving the filtration competence of a filter [8]. Several polymers such as poly (vinyl pyrrolidone) which used to create fiber

Poly(vinyl pyrrolidone) (PVP) is a polymer with high biocompatibility, small chemical toxicity, in greatest organic solvents it has excellent solvability, well spin ability [5]. As well as poly(vinyl pyrrolidone) (PVP) is hygroscopic powder, a white and it is a weak characteristic order, the structural formula of

could be adjusting by proper control of electrostatic forces [3]. The device used for electrospinning method is humble in building. It involves of a syringe, high voltage source, a pump to transport the solution to the syringe then conducting collector. Where the conducting collector might be of any form based on the obligation such as rotating drum, flat plate, etc as shown in figure (1) [4].

PVP is (C<sub>6</sub>H<sub>9</sub>NO)<sub>n</sub> [9]. Silver (Ag) nanoparticles doped with polymer solution of PVP at produce electrospun fibers were well prepared which display good antimicrobial [10,11] and adding AgNPs to polymer solution of PVP worked on increasing fibers diameter because of vacancies are filled by silver nanoparticles (AgNPs) which lead to expanded [12].

## EXPERIMENTAL WORK

### Materials

Poly (vinyl pyrrolidone) (PVP K-30), Molecular weight (40,000). Ethanol is solvent colourless and the purity it 99.9% made in Spain and silver nanoparticles (AgNPs) made in USA. The particles size in the range of (50-80)nm

### Preparation of polymer solution of PVP/Ag nanoparticles

Polymer solution of PVP was prepared via dissolving 8gm PVP (MW40,000) powder in 50 ml ethanol alcohol at room temperature via stirrer device during 30 minutes according to the following equations [9].

$$C_x = \frac{n_x}{v} \quad (1)$$

$$n_x = \frac{m}{M.W} \quad (2)$$

Where

C<sub>x</sub> is the concentration (mol/L)

n<sub>x</sub> is the number of mole

v is the volume of solvent (liter)

m is the mass of PVP(g)

M.W is the molecular weight(g/mol)

0.1AgNPs was added to PVP/ethanol with incessant stirring for 1h at room temperature. Then sample of polymer solution of PVP put in plastic syringe where used electrospinning device, the syringe have needle is inside diameter 0.48mm, also connected to voltage power source, The feed rate of the polymer solution of PVP was controlled at 1mL/h via a syringe pump, where a piece of grounded silicone used as the collector. The distance between the needle and collector was 15cm also the applied voltage was 15KV.

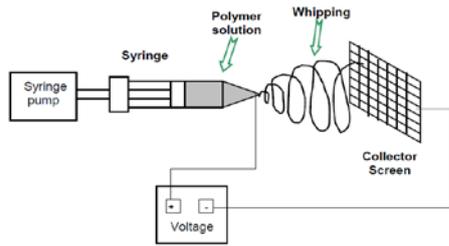


Figure 1: shows electrospinning system

2. RESULTS AND DISCUSSION

X-ray diffraction of PVP powder

The X-ray diffraction examination showed that PVP powder has two peaks at  $2\theta$  equal to  $11.6417^\circ$  and  $20.8742^\circ$ , appearance number of peaks to article PVP indicating that the article is installation of a multi-gelling, also intensity (Count) equal to 57.90 and 53.53 in the range  $5^\circ$  to  $80^\circ$ . This conformity with reflects the nature of this pure PVP and standard for this polymer. These results agreement with researcher's results M.T.Razzak [13]. As shown in figure(2). The average grain volume ( $D_{av}$ ) of PVP equal to 3.15nm which determined via using scherrer's relation.[14]. As shown in the flowing equation

$$D_{av} = \frac{0.9\lambda}{\beta \cos\theta} \tag{3}$$

$\theta$  is angle diffraction Brac,  $\lambda$  is the wavelength of X-ray which used,  $\beta$  is (FWHM), 0.9 is shape factor, FWHM is Full Width at half maximum value

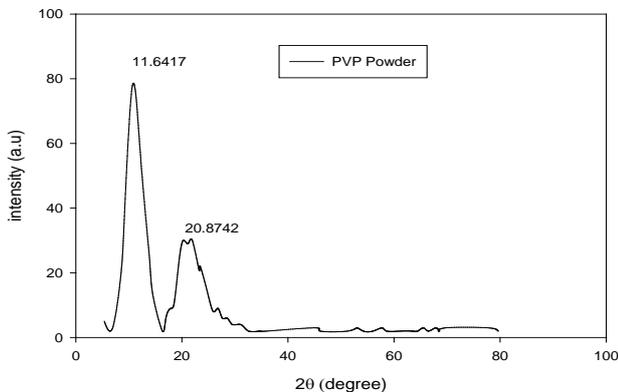


Figure (2): Shows X-ray diffraction of PVP polymer

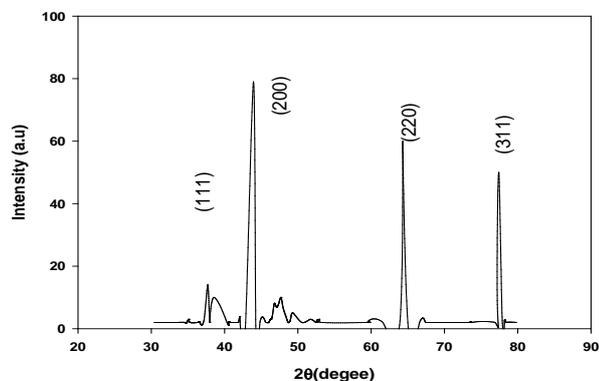


Figure (3) : Shows X-ray diffraction of silver nanoparticles (AgNPs) film

X-ray diffraction of silver nanoparticles ( AgNPs)

The X-ray diffraction examination showed that AgNPs powder have three peaks at  $2\theta$  equal to  $43.953^\circ$ ,  $64.313^\circ$  and  $77.432^\circ$ , appearance number of peaks to article AgNPs indicating that the article is installation of a multi-gelling [13]. And intensity (Count) equal to 79, 60 and 50 in the range  $30^\circ$  to  $80^\circ$ . The crystal structure of silver nanoparticles is face-centered cubic. As it appeared coefficients Miller values is (111),(200),(220)and (311) respectively this conformity with reflects the nature of this pure AgNPs. This results agreement with the result of researcher [15], the average grain volume ( $D_{av}$ ) of AgNPs equal to 23.6 nm which determined via using scherrer's relation [14]. Figure (3) shows the measure of X-ray diffraction of AgNPs powder.

Atomic Force microscope (AFM) of silver nanoparticle (Ag NPs)

The size and shape of AgNPs was synthesized via Atomic Force Microscope (AFM). Figure (4) verifies that AgNPs were less or more homogenous in size also spherical form. The measured height is expected to be as large as the width assuming a spherical nanoparticle shape [16]. The roughness average of AgNPs is 35.3nm. Also Figure (5) show AFM Distribution of volume AgNPs

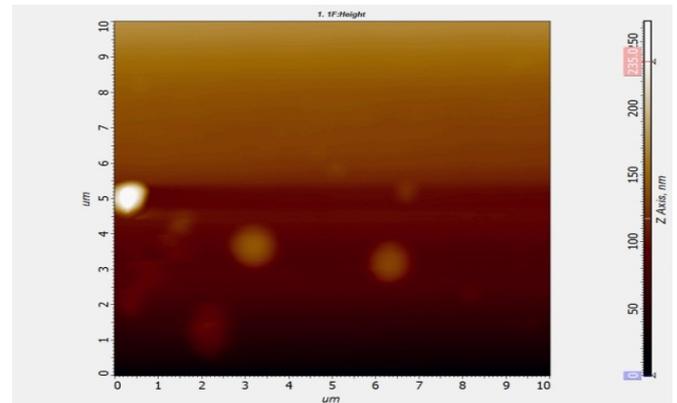


Figure (4) shows AFM measurement of silver nanoparticle (AgNPs)

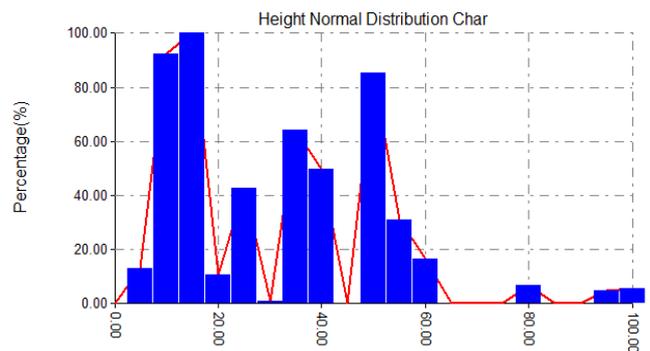


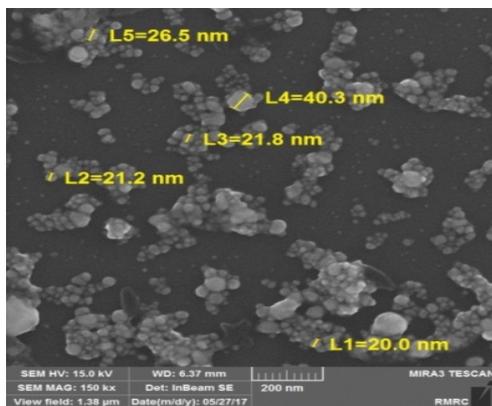
Figure (5): AFM Distribution of volume AgNPs

Scanning Electron Microscope (SEM) of silver nanoparticles (AgNPs)

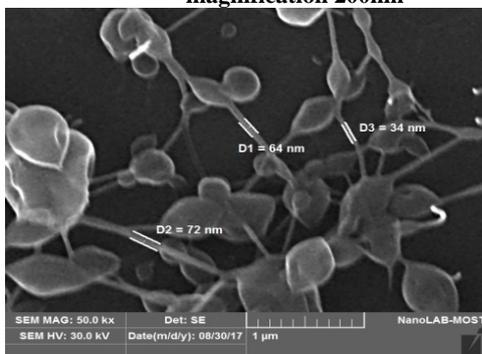
Structural, size and morphology properties of used AgNPs were characterized by SEM shown that these particles have size in the range from (20.0 to 40.3)nm. As well as AgNPs which deposition on pieces of silicon appeared spherical by SEM measurement which agreement with the researcher Muhammed Akram Raza et al. [17]. As shown in Figure (6)

**Scanning Electron Microscope (SEM) of model consisting from 0.004 PVP/ethanol and (0.004PVP+0.1wt%AgNPs)/ethanol**

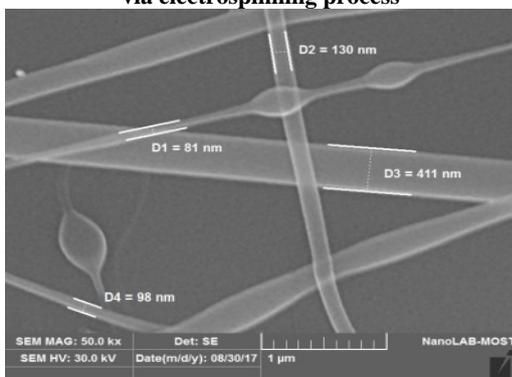
Figure (7) shows SEM images of pure PVP /ethanol nanofibers prepared via electrospinning process . The diameter of nanofiber is in the range (34 to72) nm in case pure PVP /ethanol. Polymer solution of PVP/ethanol can be produced smooth nanofibers because of low surface tension [18]. This is due to progress in fiber, which is according to coulomb force as well as causes a growth in the length of the fiber to its width ,leading to thinning of the fiber and fewer fiber diameter output[19]. Figure (8) shows SEM images of pure PVP/AgNPs in ethanol nanofibers prepared via electrospinning process. The diameter of nanofiber is in the range of (81 to 98)nm. It was noticed an increasing in the applied voltage lead to in decrease fiber diameter and lesser probability of beading, either when increasing feed rates lead to increase in bead generation, also decrease in fiber diameter with low feed rate . High viscosity worked with disappearance beads and decrease in fiber diameter [20].



**Figure (6) : Shows SEM of silver nanoparticles at magnification 200nm**



**Figure(7) shows SEM images of pure PVP /ethanol prepared via electrospinning process**



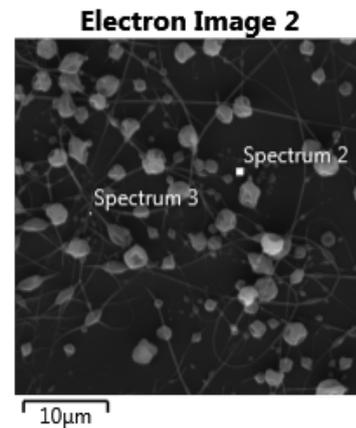
**Figure (8) shows SEM images of model consisting from ( PVP/AgNPs) /ethanol prepared via electrospinning process**

**Energy Dispersion Spectroscopy (EDS)**

Analysis of samples of (0.004PVP+0.01wt%AgNPs) /ethanol via using EDS measurement and showed results which listed in the Table (1), where figure (9) show EDS analysis of PVP nanofiber /ethanol

Table (1) represents EDS analysis and percentage of the elements of the sample which consisting from( 0.004 PVP+0.1wt% AgNPs) /ethanol and deposition on the pieces of silicon

Spectrum Label	C	O	Si	Ag	Total
1) Spectrum2	39.15	1.33	59.52	0.00	100.00
2)Spectrum3	28.00	1.07	70.90	0.03	100.00



**Figure (9): Shows EDS analysis of (0.004PVP+0.1wt%AgNPs) /ethanol at magnification 10μm.**

**3-CONCLUSION**

The morphology and structural properties of PVP nanofibers showed an influence of AgNPs on fiber morphology. PVP/AgNPs solutions of nanofiber produced nanofibers have large size from in case pure PVP nanofiber because of the vacancies between the polymer chains are filled by AgNPs which led to expand . The pure PVP nanofibers and PVP nanofiber doped by silver nanoparticles (AgNPs) showed different range in diameters which have a diameter ranging (34 to72)nm and (81 to98) nm respectively

**ACKNOWLEDGMENT**

We would like to thank Department of Physics at Faculty of Education for Girls and Faculty of Science at University of Kufa /IRAQ .

**REFERENCES**

- [1] Bourourou ,M., Holzinger,M., Bossard,F., Hugenell,F., Maaref,A. and Cosnier,S.(2015) "Chemically reduced electrospun polyacilonitrile-carbon nanotube nanofibers hydrogels as electrode material for bioelectrochemical applications", Carbon , , 87: p. 233–238.
- [2] Hong, K.H.(2007) "Preparation and properties of electrospun poly(vinyl alcohol)/silver fiber web as wound dressings", Polym. Eng. Sci., 47: p. 43–49.
- [3] Baptista , A.C., Botas, A.M ., Almeida, A.P., Nicolau,A.T., Falcão ,B.P., Soares, M.J., Leitão,J.P., Martins,R., Borges, J.P. and Ferreira, I.(2015) "Down conversion photoluminescence on PVP/Ag-nanoparticles electrospun composite fibers", Opt. Mater.( 39: p. 278–281.
- [4] Subbiah,T., Bhat, G.S., Tock ,R.W., Parameswaran,S., Ramkumar,S.S. "Electrospinning of nanofibers", Journal of Applied Polymer Science, (2005) , 96(2): p. 557-569.

- [5] Nasouri, K., Shoushtari, A.M. and Mojtahedi, M.R.M." ( 2015) Effects of polymer/solvent systems on electrospun polyvinylpyrrolidone nanofiber morphology and diameter", *Polym. Sci. Ser.* , 57: p.747–755.
- [6] Nasouri, K., Shoushtari, A.M. and Mojtahedi, M.R.M." ( 2015) Evaluation of effective electrospinning parameters controlling polyvinylpyrrolidone nanofibers surface morphology via response surface methodology", *Fibers Polym* , 16: p.1941–1954.
- [7] Dersch, R., Steinhart, M., Boudriot, U., Greiner, A. and Wendorff, J.H.(2005) "Nanoprocessing of polymers: applications in medicine, sensors, catalysis, photonics", *Polymers for Advanced Technologies*, 16 (2-3): p.276 -282.
- [8] Huang, Zheng, M., Zhang, Y., Kotaki, M. and Ramakrishna, S.(2003)"A review on polymer nanofibers by electrospinning and their applications in nanocomposites", *Composites Science and Technology*, 63(15): p.2223 – 2253.
- [9] Skoog, D.A., West, D.M., Holler, J.F., Crouch, S.R. and Holler, C.(2012) "Fundamentals of analytical chemistry", 9th edit, Boston, MA, United States, Wadsworth Publishing Co.,
- [10] Jia, Y., Huang, G., Dong, F., Liu, Q. and Nie, W.(2015) "Preparation and characterization of electrospun poly( $\epsilon$ -caprolactone)/poly(vinylpyrrolidone) nanofiber composites containing silver particles.*Polym. Compos.* . [CrossRef]
- [11] Wang, S., Bai, J., Li, C., Zhang, Y. and Zhang, J." (2012) Ag nanoparticle-embedded one-dimensional-CD/PVP composite nanofibers prepared via electrospinning for use in antibacterial material", *Colloid Polym. Sci.* ( ),290:p. 667–672.
- [12] Ron, K.(2014) "Factors Affecting Density of Matter", School for Champions ,
- [13] Razzak, M.T., Zainuddin, Dewi, S.P., Lely, H. and Taty, E. (1999) "The characterization of dressing component materials and radiation formation of PVA–PVP hydrogel", *Radiation Physics and Chemistry* 55(2): p. 153– 165.
- [14] AL.Shammary,N.F. (2010)"Optical characteristics of NiO Thin Film on Glass Formed by Chemical spray pyrolysis", *Journal of Kufa – Physics*2, 1),
- [15] Heidarpour, F., Wanab,W.A., Mozafari, M.R. , Bin Ahmadun,F.R., Sobri,S., Zargar ,M. and Karim,G., (2011)"Nano Silver-Coated PolyPropylene Water Filter :I.Manufacture By Electron Beam GUN Using amodified Balzers 760 Machine " ) ,5 :p.787-796.
- [16] Uma,R.S.,Sudipta, K.M., Mohd,S.A. , Sudipta ,K.M. and Mallappa, K.S.(2015) "Synthesis and characterization of silver nanoparticles using Fruit extract of Momordica cymbalaria and assessment of their in vitro antimicrobial antioxidant and cytotoxicity activities ", *spectrochimica Acta PartA: Molecular and Biomolecular Spectroscopy* p.939-944
- [17] Mohamed, A.R., Zakia ,K.,Anum,R.,Anjum,N.,Saira,R . and Shahzad ,N.(2016) "Size- and Shape- Dependent Antibacterial studies of Silver Nanoparticles synthesized by Wet Chemical Routes", *Nanomaterials* , 6(4) :p.5-6.
- [18] Fong, H., Chun, I. and Reneker, D. H. (1999)" Beaded nanofibers formed during electrospinning", *Polymer.* ( ), 40: p. 4585-4592.
- [19] Ji , H. H., Yu, Q. W. and Jian,Y. Y.(2008) " Effect of Concentration on Electrospun Polyacrylonitrile (PAN) Nanofibers", *Fibers and Polymers*,( ) , 9 (2): p.140-142.
- [20] Bashar, H.(2011)" Controlled deposition and alignment of electro spun PMMA-g- PDMS nanofibers by novel electrospinning setups", (M.Sc. Thesis, KTH Chemical science and Engineering, Stockholm, Sweden)