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The Effects of Operating Parameters on The Morphology of Electrospun Polyvinyl alcohol Nanofibres

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Abstract :

In this research, the preparation of PVA membranes by electrospinning was studied. The influence of processing parameters, i.e., applied voltage, flow rate and spinneret-to-collector distance was investigated. More comprehensive characterizations of the nanofiber membranes, including fiber diameter, by statistical determination from (SEM) images. PVA was dissolved in distilled water at concentration (10% wt). The polymer solution was electrospun under processing conditions i.e., an applied voltage of (5,10,15,20,25) KV, a needle tip- collector distance of (4,8,12,15,20,22) cm, and a flow rate of (0.2,0.5,0.8,1,10) mL/hr, ,using orifice size of spinneret is (0.6 mm), stationary substrate set-up, aluminum collector .When the high voltage is increased with constant other parameters, the electrostatic force will increase until the polymer surface tension is overcome, allowing a charged jet of polymer to escape from the tip of needle and travel to the collector. The best applied voltage obtained is (25 KV).When the flow rate is increased with keeping other parameters constant, more polymer solution is ejected. Increasing the flow rate too high, more smooth flattened fibers and merged. In accordance with obtained results, the optimum solution flow rates were obtained to be (0.2ml/h) and (0.5ml/h).The effect of needle tip-collector distance, was studied by a series of experiments were carried out with constant other parameters. Shows that average fiber diameter have a slight decrease trend from (857 nm) at distances of (4cm) to (600nm) at distance of (22cm). Possibly the larger distances increase flight time of the jet, stretching of the solution so the solvent had enough time to evaporate completely.

Keywords: **electrospinning**;Biomaterials: Polyvinyl alcohol; Electrospinning; High Voltage; Flow Rate

الخلاصة

في هذا البحث تم تحضير انسجه من البولي فينيل الكحول بطريقة البرم الالكتروني حيث تم دراسة تأثير العوامل التشغيلية و منها الفولتية المسلطة ، معدل التدفق للسائل البوليمري والمسافة بين الابرة الي الجامع.تم اجراء بعض الفحوصات الشاملة للانسجه البوليمرية النانويه تتضمن قطر الليف بالحسابات الاحصائية من صور المجهر الالكتروني الماسح.البولي فينيل الكحول تم اذابته في ماء مقطر بتركيز (10%). المحلول البوليمري برم الكترونيا في ظروف عملية مثل الفولتية المسطله (25,20,15,10,5) كيلوفولت، المسافة بين حافة الابرة والجامع (22,20,15,12,8,4) سم ومعدل التدفق (10,1,0.8,0.5,0.2) مل.ساعه-[1]،القطر الداخلي للابرة المستخدمة (0.6 سم)،الجامع للالياف هو صفيحة المنيوم. عند الزيادة

الفولتية العاليه المسلطه بثبوت الظروف الاخرى يلاحظ تزداد ان القوة الكهروستاتيكية الى ان تتجاوز الشد السطحي للبوليمرحيث يسمح نفث البوليمر للنفاذ من حافة الابرة ليصل الى الجامع.عند زيادة معدل التدفق مع ثبوت العوامل الاخرى، أن فولتية مسلطه عاليه بقيمة 25 كيلو فولت تنتج أفضل.بزيادة معدل تدفق السائل البوليمري يحصل زيادة كميات تدفق السائل البوليمري اما عند زيادة عالية جدا لمعدل التدفق تنتج الياف مسطحة .تاثير المسافة بين حافة الابرة والجامع بثبوت الظروف الاخريلاحظ معدل قطر الليف يقل تدريجيا من (857نانومتر) على مسافة (4 سم) الى (600نانومتر) على مسافة (22سم)، حيث ان المسافة الكبيرة تسمح للمذيب بوقت اطول للتبخربشكل كامل واستطاله اكثر للالياف.

1. INTRODUCTION

Fibres of synthetic polymers have been produced for decades by conventional processes, such as melt spinning, dry spinning, and wet spinning. These techniques rely upon pressure-driven extrusion of a viscous polymer fluid [1]. Electrospinning is a novel process for forming fibers with nano-scale diameters through the action of electrostatic forces. In a typical process an electrical potential is applied between droplet of polymer solution, or melt, held through a syringe needle and a grounded target. Electrostatic charging of the droplet results in the formation of the well-known Taylor cone. When the electric forces overcome the surface tension of the droplet from the apex of the cone, a charged fluid jet is ejected [2]. The jet exhibits bending instabilities due to repulsive forces between the surface charges, which is carried with the jet, and follows a looping and spiraling path [3, 4].The electrical forces elongate the jet thousands of times and the jet becomes so thin. Ultimately, the solvent evaporates, or the melt solidifies and very long nanofibres are collected on the grounded target [2]. The morphology and diameter of electrospun nanofibres are dependent on a number of processing parameters that include: (a) the intrinsic properties of the solution such as the type of polymer and solvent, polymer molecular weight, viscosity (or concentration), elasticity, conductivity, and surface tension [5-10]. (b) the operational conditions such as the applied voltage, the distance between spinneret and collector (tip-target distance), and the feeding rate of the polymer solution [8, 11, 12]. In addition to these variables, the humidity and temperature of the surroundings may also play an important role in determining the morphology and diameter of electrospun nanofibres [13]. For instance, the polymer solution must have a concentration high enough to cause polymer entanglements yet not so high that the viscosity prevents polymer motion induced by the electric field. The solution must also have a surface tension low enough, a charge density high enough, and a viscosity high enough to prevent the jet from collapsing into droplets before the solvent has evaporated [14].

Son et al. showed that, the average diameter of poly(ethylene oxide) (PEO) nanofibres decrease with increasing PEO solution conductivity and solvent polarity [7]. Son et al. reported that, the average diameter of cellulose acetate (CA) nanofibres was not significantly changed by changing operating parameters, but increases by increasing CA solution concentration [8].

Zhang et al. found that, with increasing applied voltage the average diameter of the poly(vinyl alcohol) (PVA) nanofibre increases slightly but the distribution of diameter of fibres is increased, and tip-target distance did not have significant effects on fibre morphology morphology [11]. Wannatong et al. reported that, in electrospinning of polystyrene (PS) solutions, at first the fibre diameters slightly decrease with increasing applied voltage, and then increase with further increase in the applied voltage [9].

Deitzel et al. found that the morphology of the PEO nanofibres is influenced strongly by parameters such as feeding rate of the polymer solution and the electrospinning voltage. At constant feeding rate, by increasing the voltage of Electrospinning, the shape of the surface is changing from what the electrospinning jet originates. Therefore, there was a decrease in the stability of the initiating jet and an increase in the number of bead defects forming along the electrospun nanofibres [12]. in the present work, evaluated the effects of operating parameters including electric voltage, solution feeding rate and tip-target distance on the morphology of electrospun PVA nanofibres.

2. Materials and Methods

2.1 Characteristics of Polyvinyl alcohol (PVA)

Polyvinyl alcohol (PVA) is the world's largest volume, synthetic, water soluble polymer. PVA is nonhazardous and is used in many adhesives, a polymer with a repeating vinyl alcohol unit and its molecular weight (80,000), Preparation of Polyvinyl Alcohol Density(1.31 g/cm^3)from Sinopharm chemical Reagent Co. (100 ml of PVA[10%]water solution] (10 gm of PVA – 90ml of distilled water)as shown in fig(1).

Important test for prepared PVA polymer solution before spinning process, carried with Electrical conductivity (Used Cand 7110 inolab), Viscosity (usingViscometer (DV-II+Pro) Brook field) and Surface Tensiometer Model (JYW -200A LARYEE TECHNOLOGY CO,).

2.2 Electrospinning process

An experimental laboratory stand for manufacturing nonwoven materials by means of the electrospinning technique was designed and constructed. a photograph of its main parts and a photograph of the electrically driven bending instability of the jet, are presented in Figure(2).

After fixing the plastic syringe (10ml) on to the pump, various experiments were performed to examine the effects of material and process parameters on the fiber morphology and dimensions. This was done by using (10% wt PVA) polymer solution by changing applied voltages, flow rates and collector-to- tip distance. Various values of voltage was used to determine lower and upper limit of voltage (5,10,15,20,25) KV which produce the nanofibers with keeping other parameters constant, the distance from tip to collector was varied(4,8,12,15,20,22) cm, and a flow rate of (0.2,0.5,0.8,1,10) mL/hr. The stand is composed of three basic elements: a high voltage generator, an upper and a lower electrode. The upper electrode serves for extruding the polymer and enables the polymer drops to achieve a suitable electric potential. The second (lower) electrode is the take-up electrode, in relation to which the electric potential of the polymer is applied, and on which the fibers are deposited during the process of manufacturing the nonwoven.

2.3 Microscopic analysis

For analysis of the morphology of the electrospun fibers, the samples were sputter-coated with Au and examined with a scanning electron microscope (SEM, VEGA). Each micrograph from an SEM scan was statically analyzed. The average fiber diameter and the periodicity of fibers were calculated and drawn as histogram to obtain the fibers diameter distribution and the average fiber diameter.

3. Experimental Results

3.1 Characteristics of Polyvinyl alcohol (PVA)

Testing the PVA water solution properties, Electrical conductivity (Used Cand 7110 inolab) obtained 1222 (µS\cm) and Viscosity (usingViscometer (DV-II+Pro) Brook field) obtained 2014 (Cp)at 19 °C temperature and surface tension (44 mN/m^2).

3.2 Characterization of electrospinning processing parameters

3.2.1 Effect of applied voltage

To investigate the effect of voltage on fiber diameters, applied voltage from (5 to 25) kV was varied for electrospinning of (10wt% PVA) solution whilst keeping other parameters constant. As the results, it was found that the diameter of electrospun fibers decreases with increasing electric

field, Figures 3 (a, b, c, d, e) illustrates the SEM images of nanofibers obtained at different voltages (5, 10, 15, 20 and 25) KV with Histogram of each them respectively. The average fiber diameter was found to decrease from (910 nm) at a voltage of (5 kV) to (50-150) nm at a voltage of (25kV) at a constant distance and flow rate. Voltages of more than (5kV) caused deformation of solution drops into the shape of (Taylor cone) and formation of fibers while below drops at the tip of the needle were observed. Also, at voltages of (5 kV), Taylor cone was not stable and few fibers, mostly merged, were seen. A possible reason that high voltages about (5 KV) make the (Taylor cone) unstable could be due to the movement of the jet causing to repel more solution down the tip of the needle, leading to less stable cone. Fiber formation will be optimum when the solution is delivered to the collector at the voltages of (25kV).

3.2.2 Effect of tip-collector distance

According to SEM images of nanofibers obtained at different distances as Figures4 (a, b, c, d, e and f) with Histogram of each them it could be noticed that by altering the distance between tip to collector, the average fiber diameter have a slight decrease trend from (875 nm) at distances of (4cm) to (250nm) at distance of (20cm) decreasing diameter by increasing distance up to (20cm)over it will increase in diameter. Possibly the larger distances increase ejection time tip-collector of the jet, stretching of the solution so the solvent had enough time to evaporate completely. Dried fibers stretched and deposited on the collector, lead to result in reducing the diameter. It was noticed that, by placing collector at distance of (8 cm) and lower from needle tip, some fibers were seen but most of them got coalition. The reason would probably be due to the decrease in ejection time tip-collector and lack of enough time for excess solvent evaporation when the jet reached the collector. By placing the collector at a distance of (22cm), some of spun fibers may fail to collect on the collector. Then conclude as too small distance can lead to “wet” fibers that fuse on the collector, also the collection distance is increased; the time for the solvent to evaporate increased and as a result, dry solid fibers are collected at the target. With increasing the distance between the needle-tip and the target, the jet underwent a larger amount of electrically driven bending or whipping instability. It was found that the optimum collection distance is (20cm). Consequently, the amount of stretching or elongation of the jet increased which results in the fiber diameter to decrease are matched with [15].

3.2.3 Effect of flow rate

To examine the effect of flow rate on diameter of as spun (PVA) nanofibers, some experiments were carried out. A concentration of (10wt %) of (PVA) solution was poured into syringe and then a spinning voltage of (15kV) and flow rates from (0.2ml/h -10 ml/h) used for feeding the solution. Tip-to-collector distance was held at (15 cm). The average fiber diameter was determined by (SEM) images, which is shown in Figure5 (a, b, c, d and e) with histogram of each it.

At the low flow rate (about 0.20-0.5 ml/hr) the electrospun fiber is cylindrical and uniform. At higher flow rates (above 0.8 ml/hr) the fiber surface is rougher and the fluid jet bents from the outset and breaks before it progresses any further. No straight segment is observed. This causes non uniform, rough surface and non cylindrical fibers and merging of fibers at crossing points [16].

In accordance with obtained results, the optimum solution flow rates were determined to be between (0.2ml/h to 0.5ml/h) because fiber are more homogenous and had narrow range of fiber diameter . but at higher feed rates (10 ml/hr) larger fiber diameters often produced like mesh structure. Solution flow rate must also be accounted for in the characterization of electrospun fibre morphology. Essentially, solution flow rate adjustments are made in order to maintain a stabilized (Taylor cone) during electrospinning , it obvious that, increasing the flow rate while maintaining the (Taylor cone) produces larger fiber diameters .

Finally the effect of variation of high voltage applied ,rate of solution feeding and distance between needle tip and collector on the members fibers diameters are shown in fig (6,7, and 8) respectively.

4. Conclusion

In this research, it was found that:

1. the diameter of PVA electrospun fibers decreases with increasing electric field due to the electrostatic force in the polymer jet become large enough to overcome the cohesive force within the jet, then the spiral motion and elongation of the polymer jet in process with higher electric field strength become more active, the pore size decrease with increase applied voltage .
2. As the collection distance is increased, the time for the solvent to evaporate increased and as a result, dry solid fibers are collected at the target. Consequently, the amount of stretching or elongation of the jet increased resulting in the fiber diameter to decrease, the pore size decrease with increase collection distance.
3. Increasing the flow rate causes to generate fibers with larger diameters because more solution was drawn from pipette tip. By increasing the flow rate too high, fibers got flattened and merged. It could be because of ejection of more solution from the tip and consequently the solvent takes a longer time to evaporate and as a result fibers merge together, the pore size decrease with increase applied voltage.

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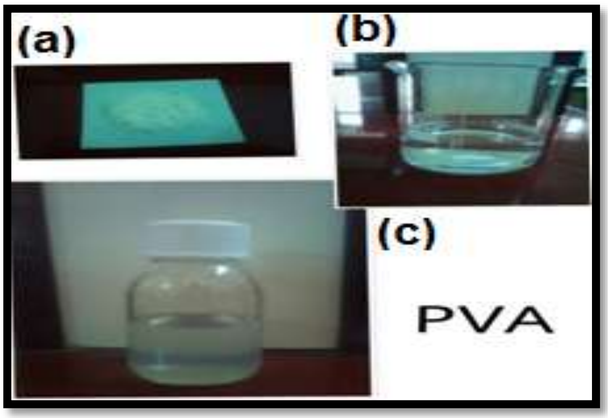


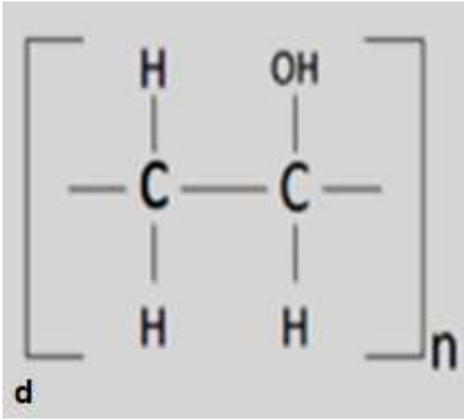


Figure (1): PVA preparation: (a) powder, (b) distilled water, (c)PVA solution .respectively-Chemical Structure of PVA which is represented by $(C_2H_4O)n$ formula.

Figure(2): **a)**Nanobond Electrospinning system with rotation collector, **b)**with flat plate collector, **c)** needle connected to high voltage by upper electrode ,.and **d)** flat aluminum plate collector connected to earthing lower electrode, with Taylor cone and spun image .

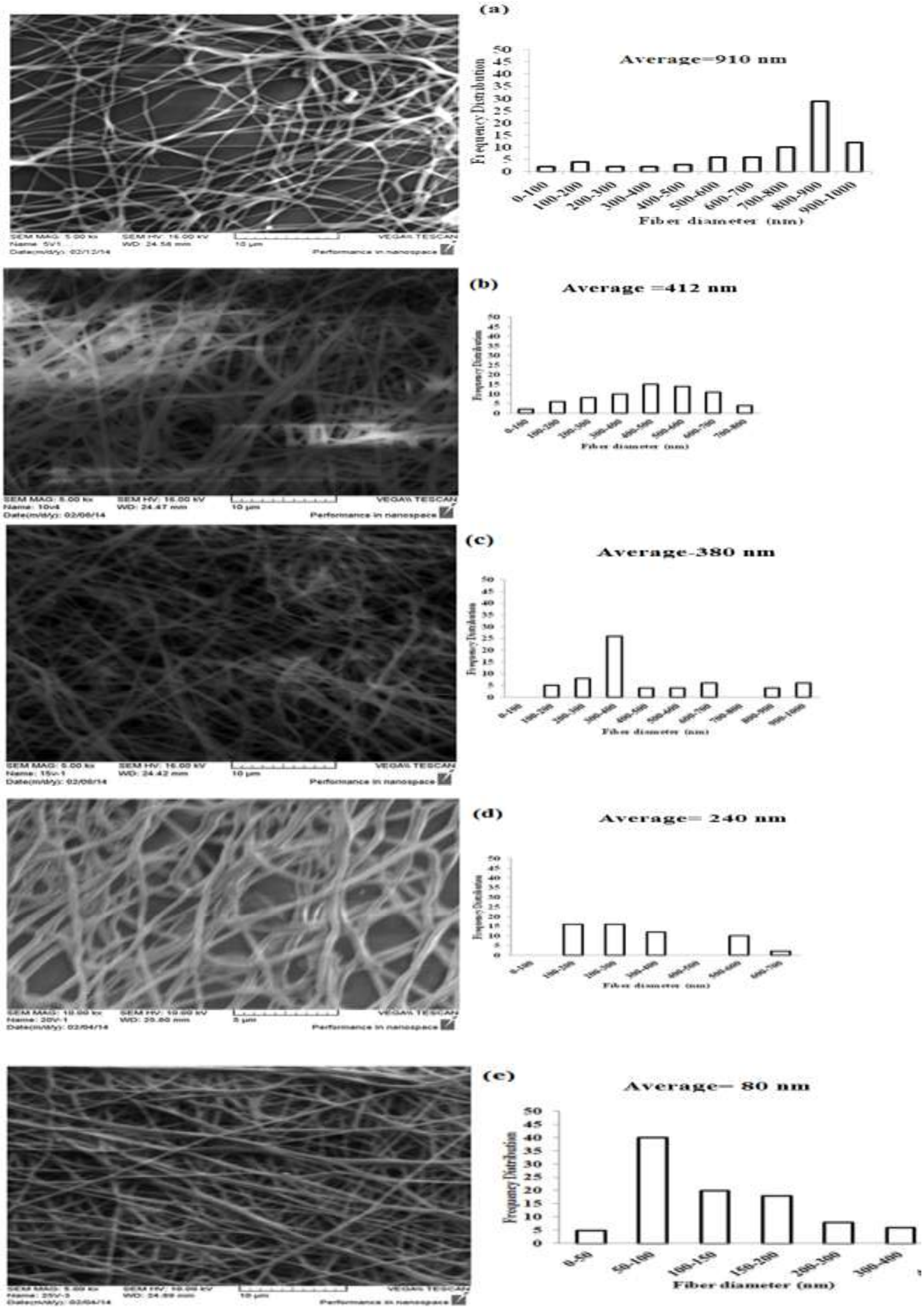
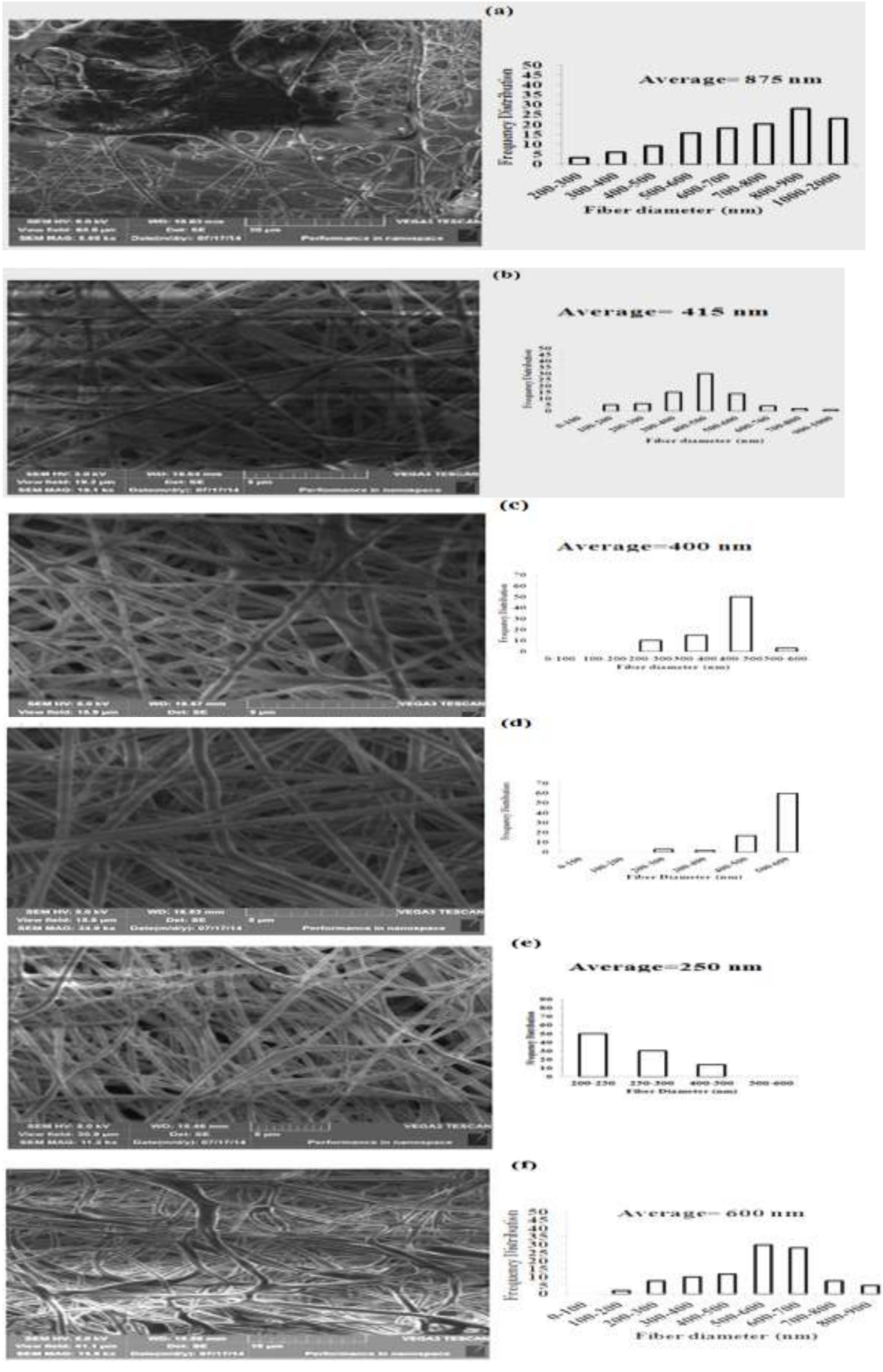


Figure (3): SEM images and histogram of PVA electrospun nanofiers with various Applied Voltages (Distance=10cm, Flow rate = 0.2 ml/hr ,Temperature = 25 C°) Voltages a) 5 KV; b) 10 KV ; c) 15 KV ; d) 20 KV ; e) 25 KV respectively .



Figures (4): SEM images of PVA nanofibers at (15KV), flow rate (0.2ml/hr) at different needle tip-collector distance a)4 cm , b) 8cm, c)12cm, d)15cm, e)20cm and f)22cm with Histogram of each them.

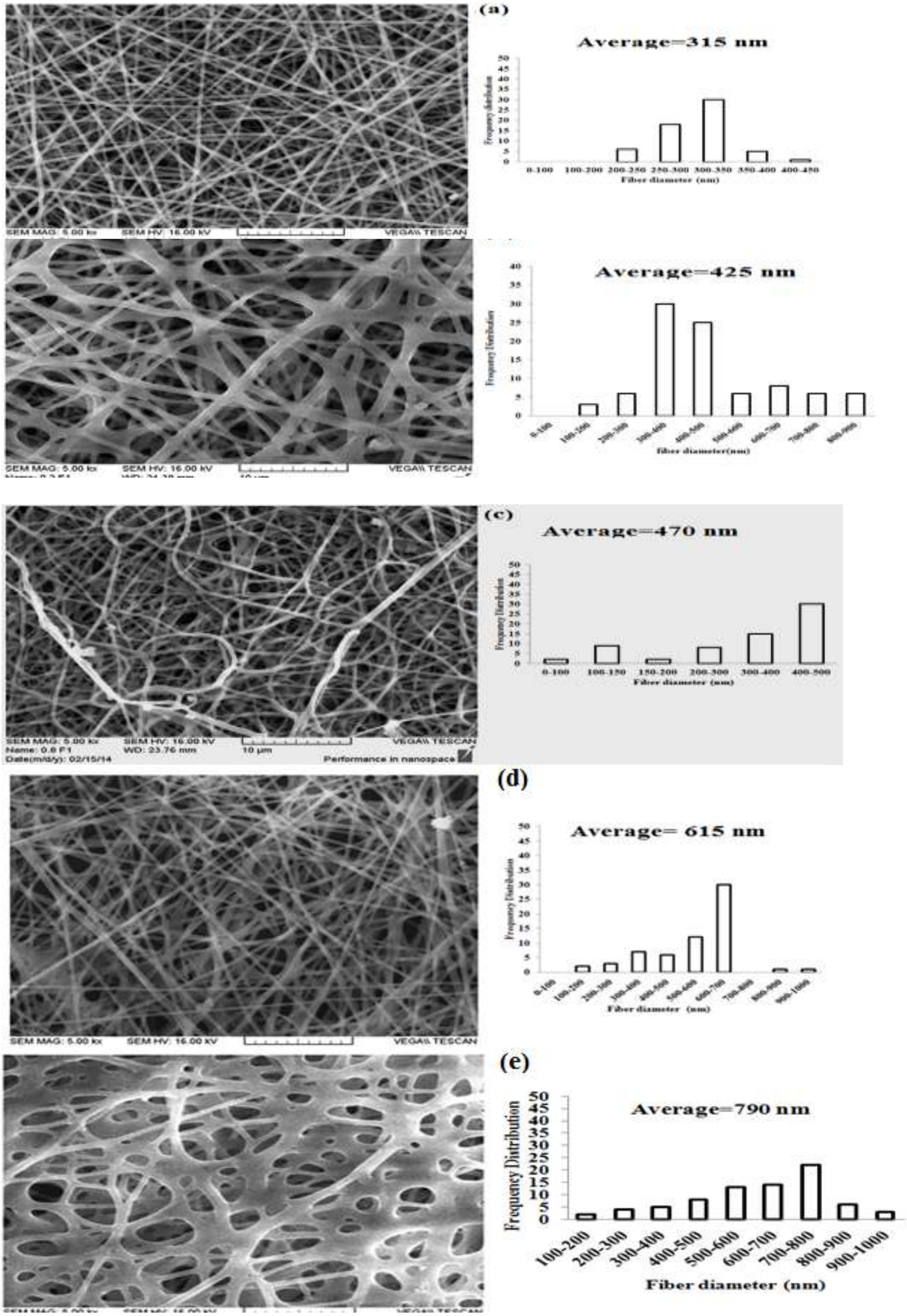


Figure (5) SEM images of PVA electrospun nanofiers with various Rates (Voltage =15 cm, Distance = 12 cm, Temperature = 25 C°) Flow rates a) 0.2 ml/hr; b) 0.5 ml/hr ; c) 0.8 ml/hr ; d) 1 ml/hr ; e) 10 ml/hr .

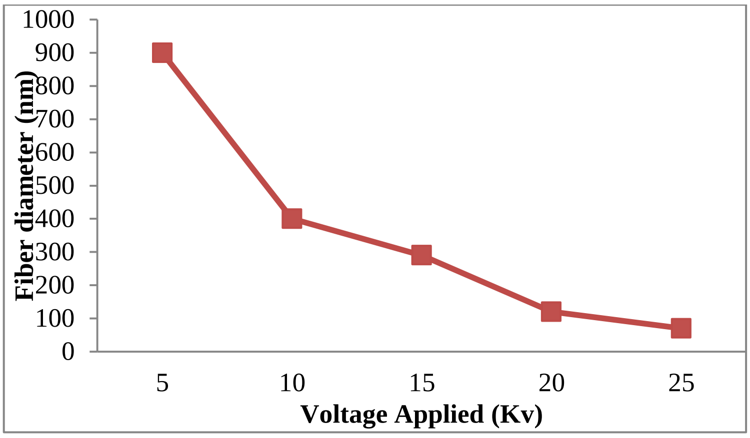


Figure (6) Effect of applied high voltages on fibers diameters.

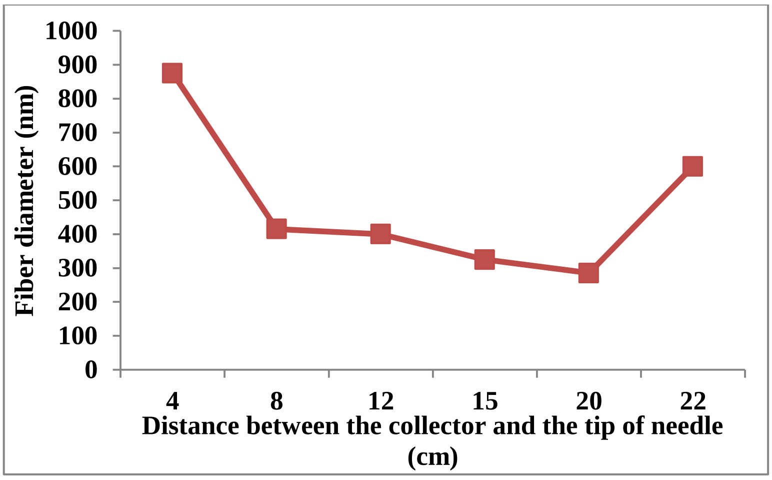


Figure (7): Effect of distance between needle tip and collector on fibers diameters.

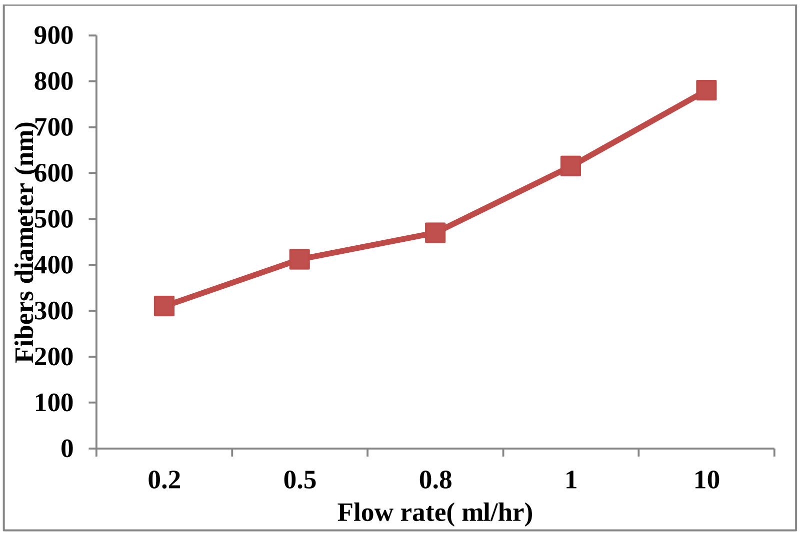


Figure (8) Effect of polymer solution feeding rate on fibers diameters .