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MORPHOLOGY CONTROLLED ELECTROSPUN POLY(VINYL PYRROLIDONE) FIBERS: EFFECTS OF ORGANIC SOLVENT AND RELATIVE HUMIDITY

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Abstract

We report the effects of various solvents and relative humidity on the morphologies of the resultant electrospun poly(vinyl pyrrolidone) (PVP) fibers during electrospinning process. The PVP solution (~10wt%) dissolved in ethanol (EtOH) exhibited the best electrospun PVP fibers, whereas water and DMF produced the film-like morphologies under the identical conditions, indicating the failure of fiber formation, mostly due to slower evaporation of the solvents, and thereby immediately re-dissolution by the water and N,N-dimethylformamide (DMF) remained. In addition, the smooth PVP nanofibers

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were successfully observed at the relative humidity of 30-40%, with the fiber diameters ranging from 960nm to 1000nm. However, at higher relative humidity = 50%, the beaded fibers were formed. As the relative humidity further increased to 70%, the resulting PVP fibers were fused and resulted in film-like morphologies. This was ascribed to re-dissolution and destruction of the fiber structures formed on the collector due to higher humidity environment.

1. Introduction

In recent years, electrospinning is becoming of great interest because not only it can produce polymer fibers with diameters in the range of nano- to a few micrometers by using an electrostatically driven jet of polymer solutions or melts, but it also has the advantages of being a very simple and cost-effective method, compared to the conventional methods [4, 6, 9, 12]. Nanofibers with their huge surface areas to volume ratio, about a thousand times higher than that of a human hair, have the potential to significantly improve current technology and find various applications in new areas [7, 10]. Up to now, majority researches on electrospun fibers have been on exploring various issues such as the fundamentals of electrospinning, electrospinning conditions [1], characterization of the fibers, and finding new applications for it. Numerous polymer systems, including homopolymers, various kinds of copolymers, blends, and composites were successfully electrospun [2, 13]. However, despite of so many researches considering the microstructure and morphological changes by manipulating many factors, such as solution parameters (solution viscosity, surface tension, conductivity, etc.), processing parameters (tip-to-collector distance, temperature, humidity, etc.) during electrospinning process, most of them were conducted under normal environmental surroundings without controlling the relative humidity. Only a few limited works were carried out to understand the fiber formation by controlling the relative humidity [3, 5, 11]. One interesting work reported by Megelski et al. [5] described that, they have been able to produce polymeric fiber with a high surface area through the introduction of a micro- and nanostructured surface structure with diameters in the range 20-350nm to larger flat pores of about 1μm, which was referred to as a “porous” morphology. It was found that the process of pore formation arising from rapid solvent evaporation most likely occurs due to the formation of water droplets from atmospheric water due to evaporative cooling of the polymer solution as they travel the distance from the syringe to the target, indicating that the solvent vapor pressure has a critical influence on the process of pore formation. Along this line, poly(N-vinyl pyrrolidone) (PVP) can be a good material to investigate the effects of both solvent and humidity on the fiber formation because of very hygroscopic and water soluble polymers. It can be also dissolved in various solvents, such as methanol, ethanol, water, and N,N-dimethylformamide (DMF), etc., which allow us to investigate the morphological changes in terms of volatile solvents and relative humidity during electrospinning process. In this paper, the goal of this study is to investigate the effects of various solvents and relative humidity on the morphologies of the resultant electrospun PVP fibers during electrospinning process.

2. Experimental

2.1. Materials

Poly(vinyl pyrrolidone) (PVP) with $M_w = 1{,}300\text{kDa}$ was obtained by Aldrich Co. Ltd. The solvents used in this work was ethanol (EtOH), methanol (MeOH), and N,N-dimethylformamide (DMF), where were purchased from Wako, Osaka, Japan. All chemicals were of analytical grade and were used without further purification. Table 1 shows the physical properties of each solvent used.

Table 1. Properties of various solvents used in this study

	Boiling temperature (^{o}C)	Surface tension (mN/m)	Dielectric constant (20^{o}C)
Methanol	64.7	22.6	32.7
Ethanol	78.4	22.3	24.3
Water	100	72.0	78.4
Dimethylformamide	153	-	43.9

2.2. Electrospinning

A high-voltage power supply (Har-100*12, Matsusada, Co., Tokyo, Japan), capable of generating voltages up to 100kV, was used as the source of the electric field. The PVP solutions dissolved in each solvent were supplied through a 5ml plastic syringe attached to a capillary tip with an inner diameter of 0.6mm. The copper wire connected to a positive electrode (anode) was inserted into the polymer solution, and a negative electrode (cathode) was attached to a metallic collector. The voltage was fixed at 10kV. The distance between the capillary tip and the collector was fixed to be 15cm. The concentration of PVP solutions was in the range of 8-12wt%. Specifically, in order to control the relative humidity during the electrospinning, a chamber was specially designed and its schematic diagram was shown in Figure 1. All solutions were electrospun onto a rotating metallic collector at room temperature in the glove box, which was controlled to keep a predetermined relative humidity during spinning process.

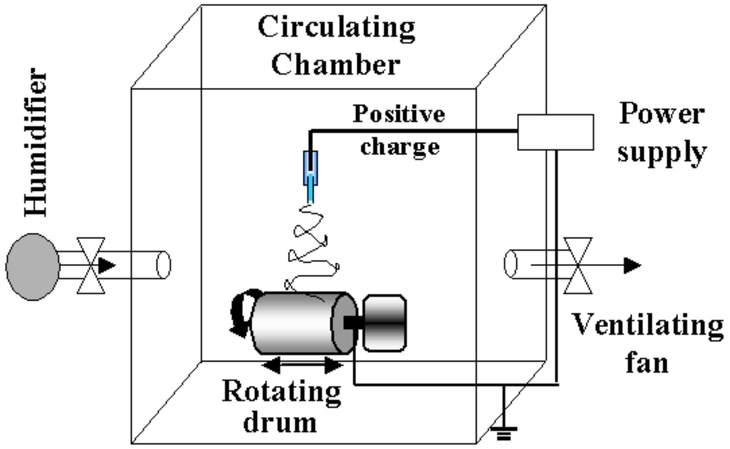

Figure 1. Experimental set-up for the humidity-controlled electrospinning.

2.3. Characterization

Solution properties, such as viscosity and surface tension, were measured with a Brookfield digital viscometer (Model DV-E) and surface tensiometer (Kruss Model K8) at room temperature, respectively. The fiber morphology, average fiber diameter, and distribution of the electrospun fibers were observed with scanning electron microscopy (SEM, VE-8800, Keyence Co., Tokyo, Japan) on samples sputtered with Palladium-Platinum. Wide-angle X-ray diffraction (WAXD) experiments were performed at room temperature with nanofiber samples using a Rotaflex RTP300 (Rigaku Co., Japan) X-ray diffractometer operating at 50kV and 200mA. Nickel filtered Cu Kα radiation was used for the measurements, along with an angular range of $5° < 2\theta < 30°$.

3. Results and Discussion

3.1. Effect of solution concentrations on fiber morphologies

In general, solution properties are one of the critical parameters in the electrospinning process, which determine the limited boundaries for the formation of electrospun fiber due to variations in the viscosity and surface tension [1, 4, 6, 13]. Therefore, in this study, the concentration of PVP solutions dissolved in ethanol as a good solvent was varied to find an optimum spinning condition of the PVP solution on electrospinning. Figure 2 shows SEM images of PVP fibers electrospun from the solutions with various concentrations. As seen in SEM images, the electrospun PVP fibers with beads and bead-string morphologies were observed at lower concentration of 8wt%, whereas the smooth and thicker PVP fibers were obtained as increasing the solution concentration due to the increased solution viscosity, which is also well coincided with the previously reported works [4, 6]. The detailed data were shown in Table 2. It was therefore concluded that the electrospun PVP fibers with smoother morphologies and narrower fiber diameter could be obtained at polymer concentration = 10wt%. Moreover, the electrospinnability was the best, and the amounts of deposited PVP nanofibers were also dramatically increased for a certain identical time.

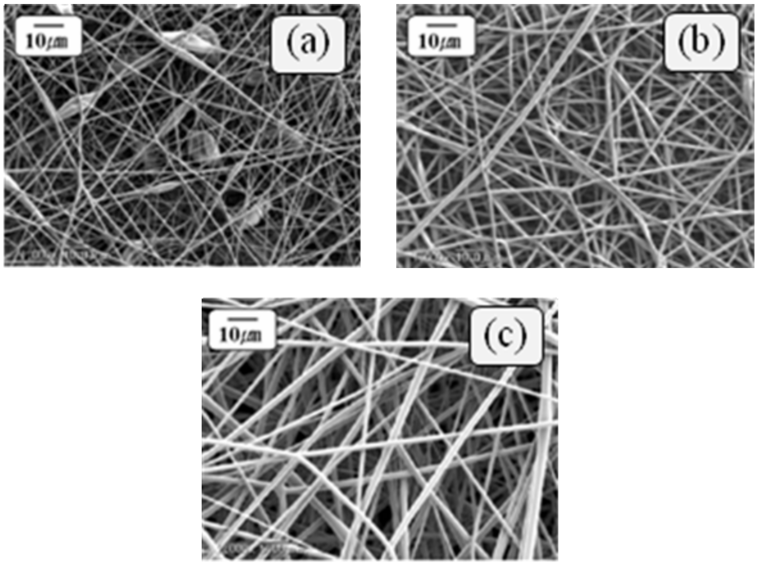

Figure 2. SEM images of electrospun PVP fibers in terms of solution concentration; (a) 8wt%, (b) 10wt%, and (c) 12wt%, respectively. The solvent was ethanol. The applied electric voltage, tip-to-collector distance, and relative humidity were 10kV, 15cm, and 30%, respectively.

Table 2. Solution viscosity and surface tension of the PVP solution dissolved in ethanol with respect to the concentration, and average fiber diameters of the corresponding electrospun PVP fibers

Concentration (wt%)	8.0	10.0	12.0
Viscosity (cPs)	122.1	174.6	446.9
Surface tension (mN/m)	22.3	22.5	23.1
Average fiber diameter (nm)	700	900	1200

3.2. Effect of solvents on fiber morphologies

Figure 3 shows SEM images of electrospun PVP fibers in terms of various solvents, such as MeOH, EtOH, water, and DMF. Here, 10wt% PVP solutions dissolved in different solvents were electrospun for 5 minutes, respectively. The other factors, such as applied electric voltage, tip-to-collector distance, humidity, were kept to be constant during electrospinning. As seen in Figure 3, the morphologies of electrospun PVP fibers were clearly different depending on the volatility of the solvents (for instance, volatility: MeOH > EtOH > water > DMF). That is, the PVP solution dissolved in EtOH, favoring the evaporation and facilitating the fiber formation, exhibited the best electrospun PVP fibers (Figure 3(b)), whereas water and DMF produced the film-like morphologies (Figure 3(c) and 3(d)), indicating the failure of fiber formation, mostly due to slower evaporation of the solvents and thereby immediately re-dissolution by the water and DMF remained. As a result, it was found that the volatility of the solvents significantly influenced the fiber formation during electrospinning and its morphologies of the resulting PVP fibers.

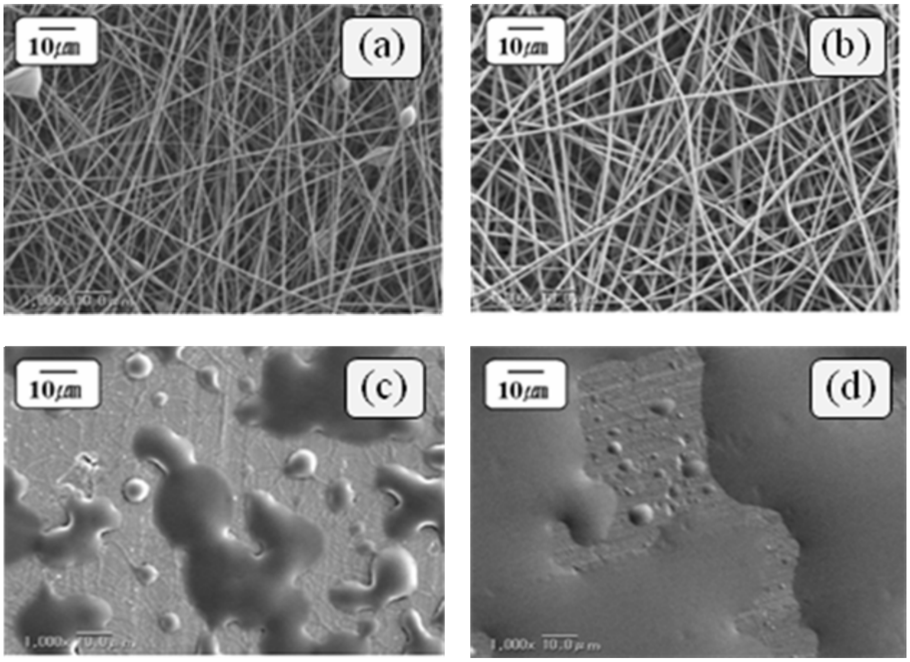

Figure 3. SEM images of electrospun PVP fibers in terms of various solvents; (a) methanol, (b) ethanol, (c) distilled water, and (d) DMF, respectively. The concentration of PVP solution was 10wt%. The applied electric voltage, tip-to-collector distance, and relative humidity were 10kV, 15cm, and 30%, respectively.

3.3. Effect of mixed solvents on fiber morphologies

It is also expected that the fiber morphologies can be controlled by mixing two solvents with different volatilities. Therefore, the PVP solutions dissolved in the mixed EtOH/MeOH solvents with various MeOH weight fractions (φ_{MeOH}) were prepared and electrospun to investigate the effects of the volatility and polarity of the solvents on the morphologies of the resulting electrospun PVP fibers. Figure 4 shows SEM images of electrospun PVP fibers in terms of φ_{MeOH}. Compared with the PVP fibers electrospun in pure EtOH solvent, all PVP fibers prepared from mixed solvents showed the bead-string fiber morphologies, irrespective of φ_{MeOH}. In addition, the fiber diameter of the resultant PVP fibers decreased as increasing φ_{MeOH} due to the decreased viscosity (Table 3).

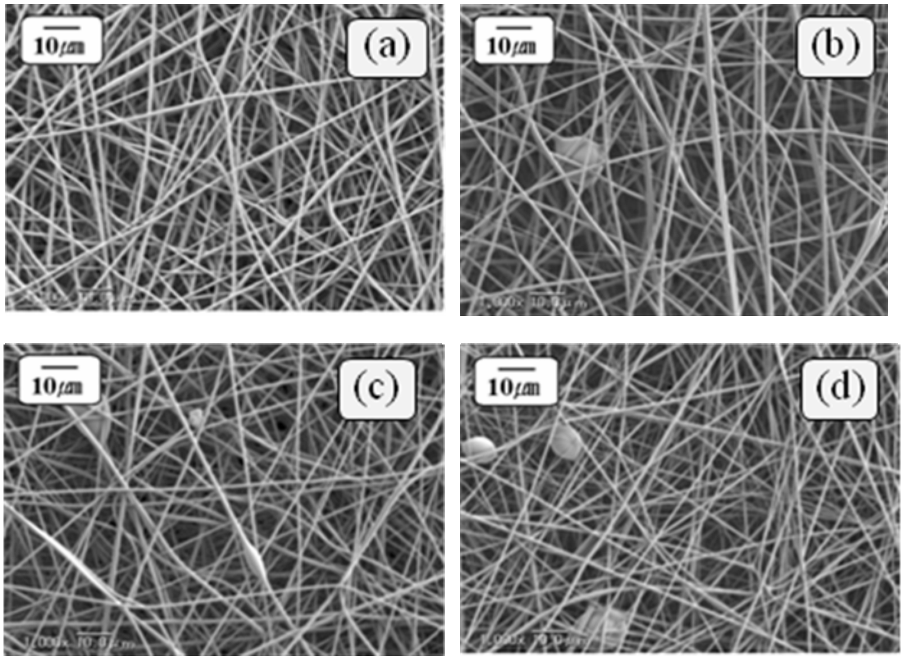

Figure 4. SEM images of electrospun PVP fibers in terms of φ_{MeOH}; (a) $\varphi_{\mathrm{MeOH}} = 0$, (b) $\varphi_{\mathrm{MeOH}} = 0.25$, (c) $\varphi_{\mathrm{MeOH}} = 0.5$, and (d) $\varphi_{\mathrm{MeOH}} = 0.75$, respectively. The electrospinning conditions were the same as in Figure 3.

Table 3. Concentration, viscosity, and surface tension of PVP solutions and their average fiber diameters of corresponding PVP nanofibers in terms of φ_{MeOH}

$\varphi_{\mathrm{MeOH}}^{*}$	0	0.25	0.5	0.75	1.0
Viscosity (cPs)	174.6	110.6	104.1	84	71.4
Surface tension (mN/m)	22.3	23.2	23.1	23	23.2
Average fiber diameter (nm)	900	840	810	720	580

*Mixed EtOH/MeOH solvents with various water weight fractions $(\varphi_{\mathrm{MeOH}})$.

Figure 5 shows SEM images of the resultant PVP fibers electrospun in the mixed EtOH/water solvents with various water weight fractions $(\varphi_{\mathrm{water}})$. The result demonstrated that φ_{water} significantly altered the spinnability and morphologies of the corresponding PVP nanofibers. Moreover, compared to the PVP fibers electrospun in pure EtOH (~900nm), the diameter of PVP nanofibers slightly decreased to about 820nm at $\varphi_{\mathrm{water}} \approx 0.25$, but further the increase in φ_{water} resulted in the formation of the bead-string fibers and nano-/micro-particles ranging from 900nm to 2.5μm in diameter, due to both decreased viscosity and increased surface tension (Table 4).

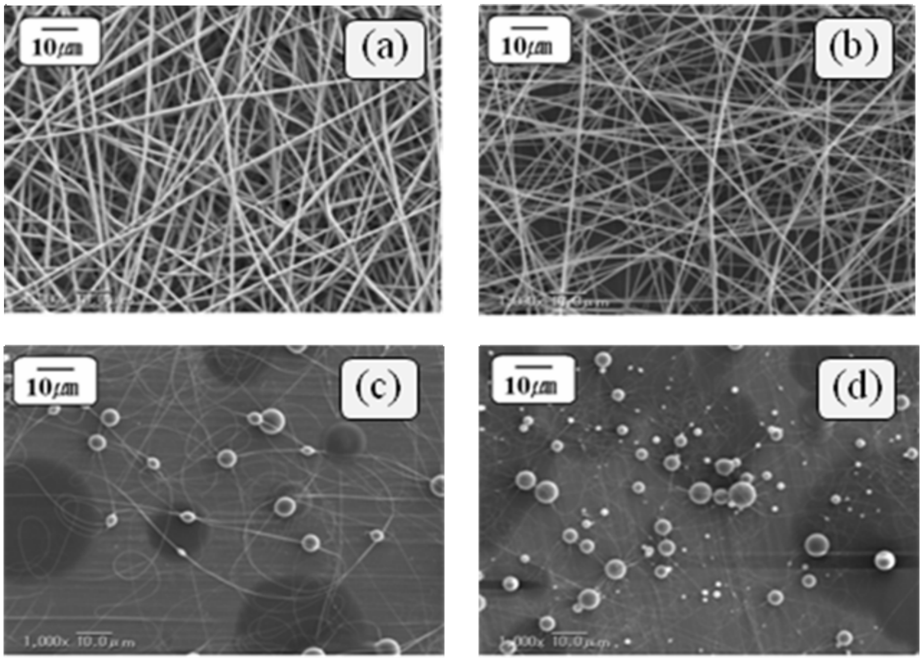

Figure 5. SEM images of electrospun PVP fibers in terms of φ_{water}; (a) $\varphi_{\mathrm{water}} = 0$, (b) $\varphi_{\mathrm{water}} = 0.25$, (c) $\varphi_{\mathrm{water}} = 0.5$, and (d) $\varphi_{\mathrm{water}} = 0.75$, respectively. The electrospinning conditions were the same as in Figure 3.

Table 4. Concentration, viscosity, and surface tension of PVP solutions and their average fiber diameters of corresponding PVP nanofibers in terms of φ_{water}

$\varphi_{\mathrm{water}}{}^{*}$	0	0.25	0.5	0.75	1.0
Viscosity (cPs)	174.6	159.6	149.7	146.7	140.5
Surface tension (mN/m)	22.3	26.4	29.6	37.0	69.7
Average fiber diameter (nm)	900	820	-	-	-

[*] Mixed EtOH/water solvents with various water weight fractions (φ_{water}).

Interestingly, at $\varphi_{\text{water}} = 0.5$, it was clearly observed the formation of nano-/microparticles. The effect of DMF (φ_{DMF}) on the morphologies of the resultant electrospun PVP fibers was also studied. The results are shown in Figure 6 and Table 5.

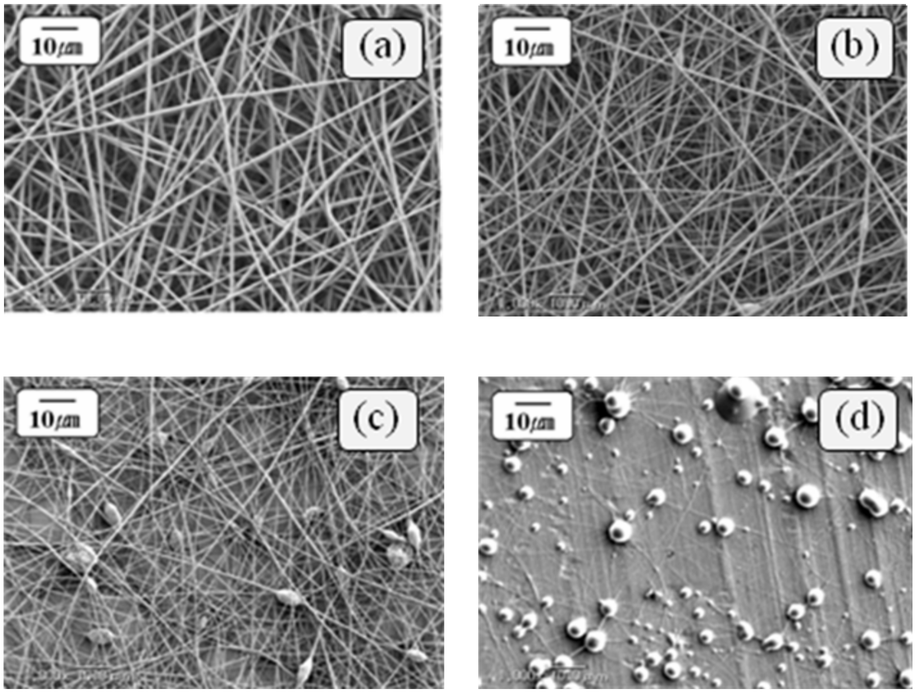

Figure 6. SEM images of electrospun PVP fibers in terms of φ_{DMF}; (a) $\varphi_{\text{DMF}} = 0$, (b) $\varphi_{\text{DMF}} = 0.25$, (c) $\varphi_{\text{DMF}} = 0.5$, and (d) $\varphi_{\text{DMF}} = 0.75$, respectively. The electrospinning conditions were the same as in Figure 3.

Table 5. Concentration, viscosity, and surface tension of PVP solutions and their average fiber diameters of corresponding PVP nanofibers in terms of φ_{DMF}

φ_{DMF}^{*}	0	0.25	0.5	0.75	1.0
Viscosity (cPs)	174.6	137.1	120	111.3	106.5
Surface tension (mN/m)	22.3	25	27.6	31.6	37.1
Average fiber diameter (nm)	900	670	390	-	-

[*] Mixed EtOH/DMF solvents with various water weight fractions (φ_{DMF}).

As increasing the φ_{DMF}, the viscosity and surface tension were decreased and thereby resulted in preferably the formation of beads or bead-string fibers. Although other researchers reported the PVP fibers without beads or bead-string fibers at lower concentration [14], but their experimental conditions during electrospinning process were different from our conditions. As a result, we found that the formation of PVP nanofibers was not affected by the polarity of the solvents, at least, in our system, but the volatility (for instance, slower evaporation) of the solvents during electrospinning process. In addition, it may be expected that such solvent property can affect the crystalline structures of the corresponding PVP nanofibers. Figure 7 shows XRD patterns of PVP nanofibers electrospun in the mixed EtOH/DMF solvents with various water weight fractions (φ_{DMF}). In case of PVP nanofibers electrospun from pure ethanol, the two diffraction peaks at $2\theta \approx 12°$ and $23°$, which correspond to the PVP crystalline phase [8], were observed. On the other hand, the relative intensity of these two peaks gradually starts to decrease as increasing φ_{DMF}, suggesting the decreased crystalline character. The obtained PVP nanofibers at $\varphi_{DMF} = 0.5$ showed amorphous character.

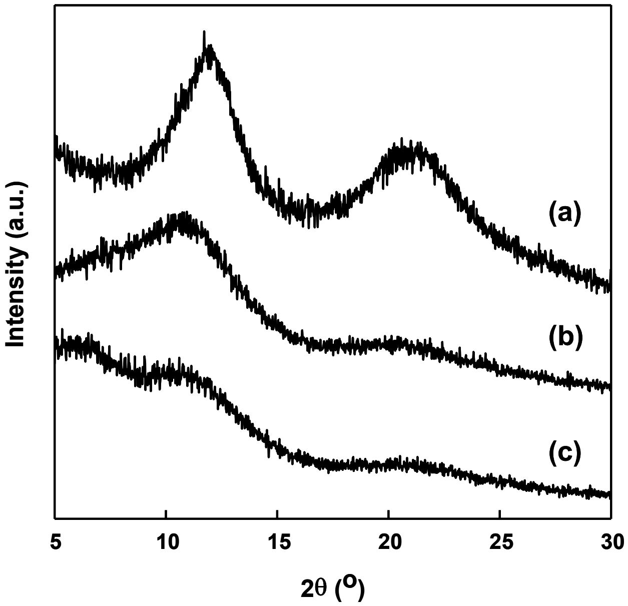

Figure 7. XRD patterns of PVP nanofibers electrospun in the mixed EtOH/DMF solvents with various water weight fractions (φ_{DMF}); (a) $\varphi_{\mathrm{DMF}} = 0$, (b) $\varphi_{\mathrm{DMF}} = 0.25$, (c) $\varphi_{\mathrm{DMF}} = 0.5$.

3.4. Effect of relative humidity on fiber morphologies

It is well known that evaporation and solidification processes in the electrospun fibers during spinning process can affect the fiber diameters, its morphologies, and microstructures. Pai et al. [5] reported that the polystyrene fibers exhibited highly porous structures in a high-humidity environment, which was a consequence of the relatively rapid diffusion of water (a non-solvent for the polymers in solution) into the jet, leading to a liquid-liquid phase separation that precedes solidification due to evaporation of DMF from the jet. In this work, the relative humidity was controlled during electrospinning process to investigate the effect of the humidity on the morphologies of corresponding electrospun PVP fibers. Figure 8 shows SEM images of the electrospun PVP fibers in terms of various relative humidity ranging from 30% to 70%. When the relative humidity was 30% and 40%, the PVP nanofibers with the diameter ranging from 960nm to 1000nm were successfully obtained (Figure 8(a) and 8(b)). On the other hand, at relative humidity = 50%, the fibers with beads started to be formed (Figure 8(c)). As the relative humidity further increased to 70%, the resulting PVP fibers were fused and produced film-like morphologies (Figure 8(d)). This was ascribed to re-dissolution and destruction of the fiber structures formed on the collector due to higher humidity environment.

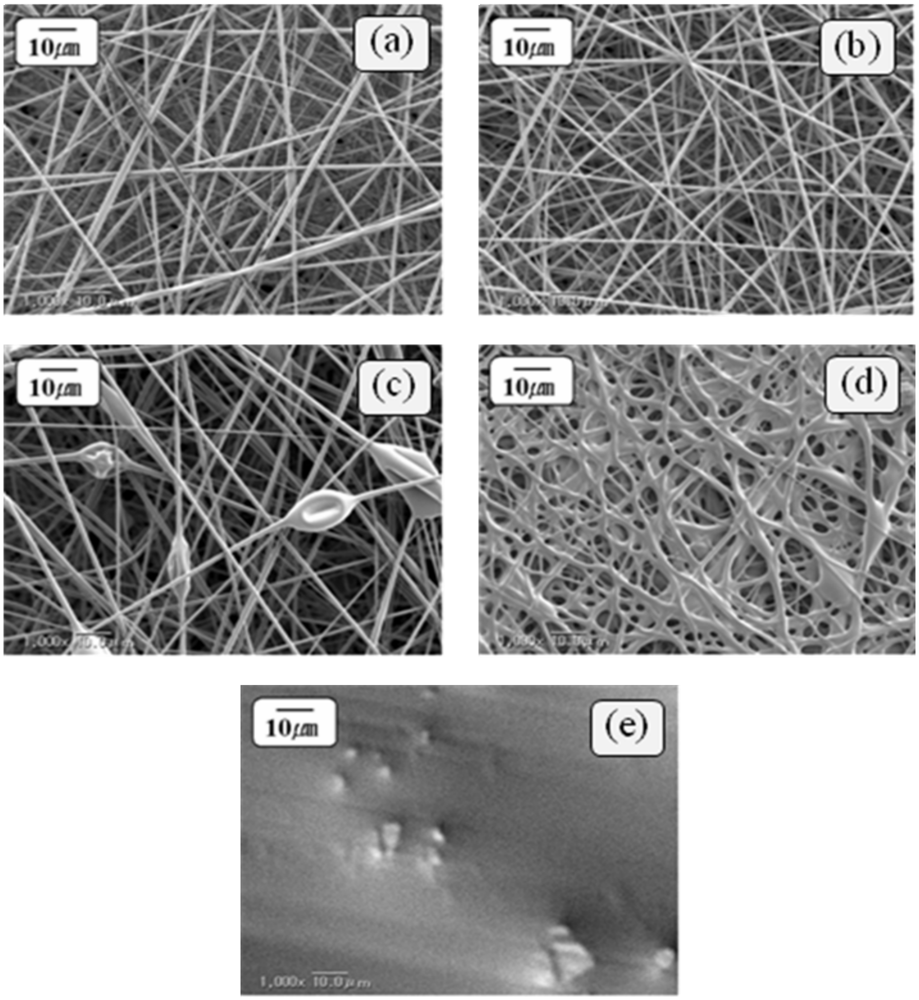

Figure 8. SEM images of electrospun PVP fibers in terms of various relative humidity; (a) 30%, (b) 40%, (c) 50%, (d) 60%, and (e) 70%, respectively. The concentration of PVP solution was 10wt%. The applied electric voltage and tip-to-collector distance were 10kV and 15cm, respectively.

4. Conclusion

We studied the effects of various solvents and relative humidity on the morphologies of the resultant electrospun poly(vinyl pyrrolidone) (PVP) fibers during electrospinning process by using scanning electron microscopy (SEM). The PVP solution dissolved in EtOH exhibited the best electrospun PVP fibers, whereas water and DMF produced the film-like morphologies, indicating the failure of fiber formation, mostly due to slower evaporation of the solvents and thereby immediately re-dissolution by the water and DMF remained. It was found that the volatility of the solvents (volatility: MeOH > EtOH > water > DMF) significantly influenced the fiber formation during electrospinning and its morphologies of the resulting PVP fibers. In addition, the smooth PVP nanofibers were successfully observed at the relative humidity of 30-40%, with the fiber diameters ranging from 960nm to 1000nm. However, at higher relative humidity = 50%, the beaded fibers were formed. As the relative humidity further increased to 70%, the resulting PVP fibers were fused and resulted in film-like morphologies. This was ascribed to re-dissolution and destruction of the fiber structures formed on the collector due to higher humidity environment.

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