

Electrospinning and The Scaling Law Model for Beaded Fiber and Smooth Fiber from Poly(vinyl alcohol) (PVA)

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Abstract

The simplicity of electrospinning technique allows production of nanofiber from various polymers and composites. In this study, we synthesized poly(vinyl alcohol)/PVA nanofiber from PVA-containing precursor solutions at three different concentrations: 5, 9 and 12% w/w. The polymer solutions were electrospun under applied voltage of 10 kV, with needle-to-collector distance of 10 cm and flow rate of 0.5 mL/hour. The resulted nanofibers were characterized for the morphology using Scanning electron microscopy (SEM) and the scaling law model. Molecular interaction within nanofiber was examined using Fourier Transform Infrared Spectroscopy (FTIR). Our findings revealed that PVA solution at 5% w/w resulted in beaded fibers with average diameter of 253 nm and the increase in PVA concentration to 9 and 12% w/w resulted in bead-free (smooth) nanofibers with higher diameter of 301 and 455 nm, respectively. The Characteristic peaks and patterns in FTIR spectra showed that hydroxyl groups (-OH) and acetate groups played an important role in the molecular interaction within PVA nanofiber.

Keywords: nanofiber, poly(vinyl alcohol) (PVA), bead fiber, fiber, diameter

Introduction

The excellent properties of nanofibers such as high surface area, fine size, porous structure, and elasticity, have made nanofibers applicable in numerous fields including drug delivery [1-2], tissue engineering [3-5] and wound dressing [6-7], supercapacitor materials [8] and many more. One of the main concerns in nanofiber production is that the fiber size should be controlled. Therefore, the method of nanofiber production should be designed in such way that the fiber size is consistent, despite the various polymer concentration.

Currently available techniques for nanofiber synthesis include drawing method, phase separation, template synthesis, self-assembly, and electrospinning. Of all those techniques, electrospinning is relatively more efficient [9]. Electrospinning is a fairly simple method to produce nanofiber from a high number of polymers and composite materials by applying Coulomb's force: the charges on the surface of ionized polymers are exposed to opposed charges from high voltage, resulting in polymer stretching and deposition in nanofiber

form [2]. Three major contributing factors to nanofiber attributes (size and morphology) should be considered: solution properties, process variables and environment variables [9,10]. One can simply predict the morphology of electrospun fiber from the viscosity and conductivity of polymer solution and processing condition.

PVA is a widely-used polymer in biomedical engineering due to its high biocompatibility, non-carcinogenicity, highly stable both chemically and thermally [1,4]. PVA has been used for nanofiber synthesis [12], yet a comprehensive study on the morphology of PVA-based nanofiber (beaded fiber and smooth fiber) and its scaling law model is still scarce. This study aimed to investigate the morphology of PVA nanofiber in relation with conductivity and to develop the scaling law model. This study also reported the presence of specific functional groups in PVA nanofiber.

Methods

Precursor solution was prepared from PVA (MW 89.000 – 98.000 g/mol) dissolved in demineralized water (Institut Teknologi Bandung, Indonesia) at concentration of 5, 9, and 12% w/w. Figure 1 illustrates the instrument setup for electrospinning process. The main components consisted of (1) syringe pump for solution loading, (2) high voltage to attract the polymer solution from the nozzle tip and (3) a rotating drum collector to collect the resulted fiber. In general, the pressure from syringe pump causes polymer solution in the syringe to move out of the syringe. The applied voltage assists the polymer solution to travel onto the collector while solidify at the same time. The solidified polymer is in nanofiber form with a high ratio of surface area to volume or mass. PVA solutions were fed into 0.6 mm syringe that has been fixed on a loading pump. The solution was spun with flow rate of 10 μ l/minute, applied voltage of 14 kV, and nozzle-to-collector distance of 12 cm.

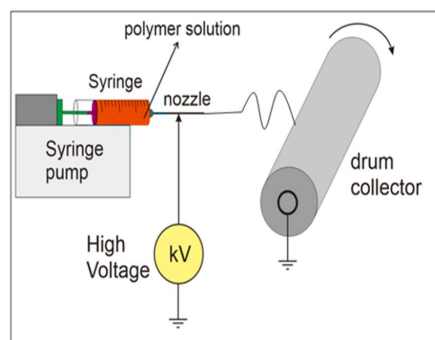


Figure 1. Electrospinning setup

Morphology of resulted nanofiber was examined using SEM (JEOL JSM-6510LV). Prior to SEM imaging, the fiber was coated with conductive carbon. SEM images were captured under excitation voltage of 15 kV and 10,000 \times magnification. The diameter of nanofiber

was determined using Image J software ($n=100$). Infrared spectrum of nanofiber was scanned using FTIR spectrometer (Alpha Platinum ATR A220/D-01) from 500 to 4000 cm^{-1} to identify the functional groups in the nanofiber.

Results and Discussion

Nanofiber Morphology as a Function of Solution Properties

Figure 2 showed the morphology of PVA nanofiber at 10,000 \times magnification. PVA solution at 5% w/w resulted in beaded fibers with average diameter of 287 nm and the increase in PVA concentration to 9 and 12% resulted in bead-free nanofibers with higher diameter of 328 and 440 nm, respectively. This is presumably associated with the viscoelastic jet break-up theory. In electrospinning process, viscoelastic force allows continuous and smooth elongation of the jet into fibers [1]. The elongation affects the movement of fiber towards the collector. In a less viscous solution, polymer chains are hardly entangled. As a result, when the fiber is exposed to high voltage, the poorly-entangled chains are easily extended and experience interrupted fiber thinning – the fiber strands break up and form beads [13]. The inertial force of the formed beads outweighs the viscous force, hence the beads are resistant to form fiber. After a certain period, this resistance may wear out and the beads can transform into fiber again, forming the beads-on-string structure [13]. The addition of highly extensible polymers into the precursor solution can improve the viscoelastic properties [1]. Therefore, higher PVA concentration, providing higher chain entanglement, resulted in beadless fibers.

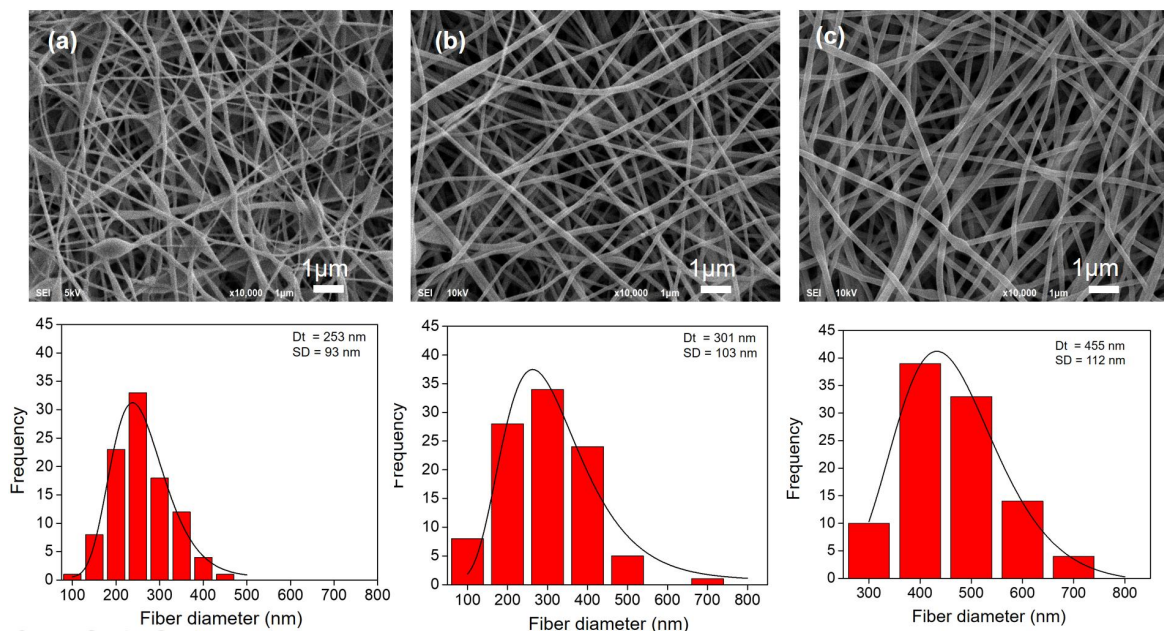


Fig.2 Morphology and size distribution of PVA nanofiber produced from PVA solution at (a) 5% w/w, (b) 9% w/w, (c) 12% w/w. Magnification 10,000 \times .

As shown in Figure 2, fiber diameter went higher as the PVA concentration was increased. The increase in fiber diameter was correlated with solution viscosity and conductivity (Figure 3), where PVA solution with higher viscosity and lower conductivity resulted in nanofiber with higher diameter. Solution viscosity indicates high degree of polymer chain entanglement, an essential factor to produce continuous fiber [3]. On the other hand, conductivity represents the surface charge of polymer solution. Low-conductivity solution has less ionized groups that can respond to high voltage. Consequently, at similar applied voltage, polymer solution with lower conductivity is more resistant to stretch out toward the collector and the resulted fiber tend to be larger [10]. This finding is consistent with former study by Munir et al (2009b) where decreased conductivity resulted in higher fiber diameter [11]. μ

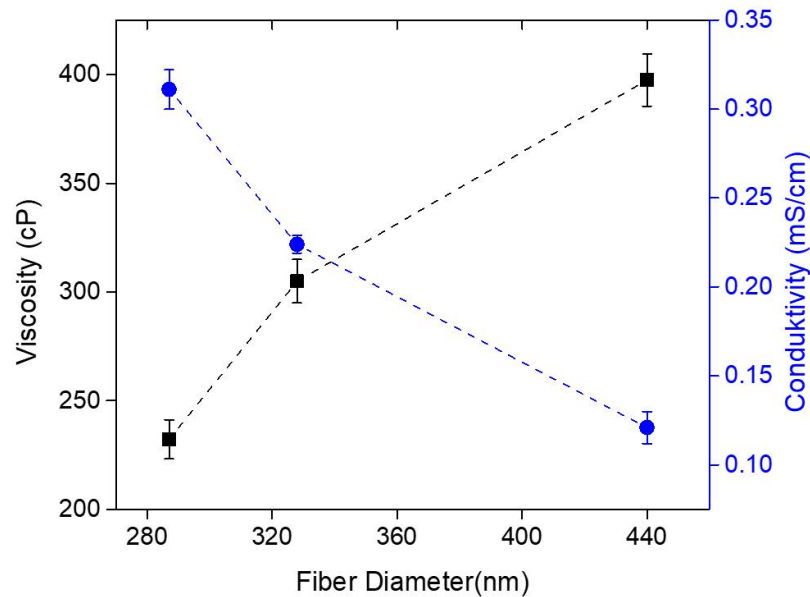


Fig 3. Correlation between fiber diameter with viscosity and electrical conductivity of PVA solution

Scaling Law Model

It has been previously reported that polymer concentration strongly influences the size and size distribution of formed particles in electrospaying. In electrospinning, as modification of electrospaying process [11], solution viscosity and conductivity should be taken into consideration in order to obtain continuous fiber [11]. These two properties can be utilized using an appropriate scaling law model to estimate the required concentration of polymer that is able to result in beadless fiber. Some of the scaling laws have been established to correlate flowrate and conductivity with fiber diameter [14,15], as described in Equation 1:

$$D_{comp} = G(\kappa) \left(\phi \kappa \epsilon_0 \frac{Q}{K} \right)^{1/3} \quad 1$$

where D_{drop} denotes the predicted diameter of the droplet, κ is the dielectric constant of the solution, ε_0 is the permittivity of a vacuum, Q is the solution flow rate, K is the solution electrical conductivity, and $G(\kappa)$ is a dimensionless function of κ [11]. $G(\kappa)$ is derived from Equation 2:

$$G(\kappa) = -10.9\kappa^{-6/5} + 4.08\kappa^{-1/3} \quad 2$$

Figure 4 illustrates the increase in particle size as a function of logarithmic of flowrate-to-conductivity ratio. The scaling law models were applied for beaded fiber and smooth fiber. The slope of the curve was obtained from Equation 3, a logarithmic form derived from Equation 1:

$$\text{Log } (D_{\text{drop}}) = \frac{1}{3} \text{Log } \frac{Q}{K} + \text{Log } [G(\kappa)(\kappa\varepsilon_0)^{1/3}] \quad 3$$

where *slope* (m) for each curve was near to constant in the right-hand side, $1/3$. We compared the curves from the current study to previous study and the findings showed that the slope in our study (0.419) did not differ markedly from the previous study by Hogan et al. (2007) at 0.3723 and by Widiyandari et al. (2007) at 0.3459. This indicates that our electrospinning process followed the theoretic model and the control of fiber size complies with Equation [14,15]. This finding also emphasizes that control of size is universal for both particle and fiber, and is highly important to predict interdependence of Q and σ on D for nanofiber.

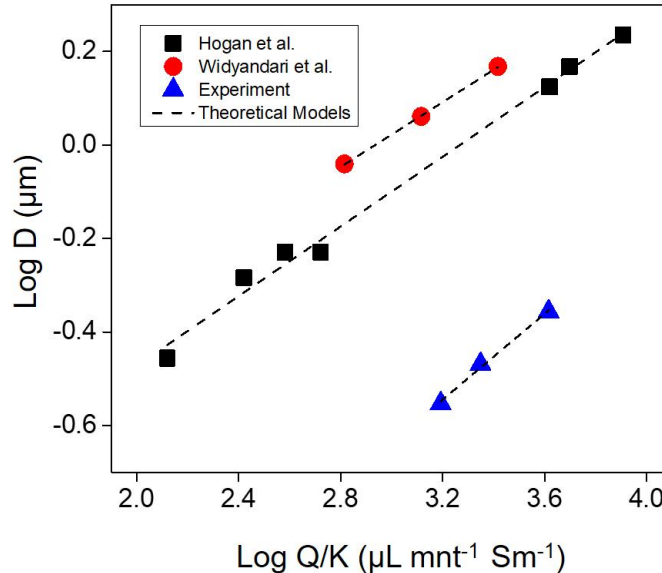


Figure 4. Relationship between fiber diameter and flowrate-to-conductivity ratio. Upper curve: beaded fiber; lower curve: smooth fiber.

FTIR

Figure 5 shows FTIR spectra of PVA nanofiber with characteristic peaks that belong to hydroxyl groups and acetate groups. The broad peak appearing at 3288 cm^{-1} was assigned for O-H stretching from intermolecular- and intramolecular-hydrogen bond. The peaks at 2937 and 2906 cm^{-1} were assigned for C-H stretching. CH_2 bending, symmetric deformation of CH_3 , C-O stretching, and C-C stretching were respectively indicated by the peaks appearing at 1440 cm^{-1} , 1373 cm^{-1} , 1093 cm^{-1} , and 850 cm^{-1} [16]. Crystallization-sensitive band of PVA nanofiber was observed at 1140 cm^{-1} [16].

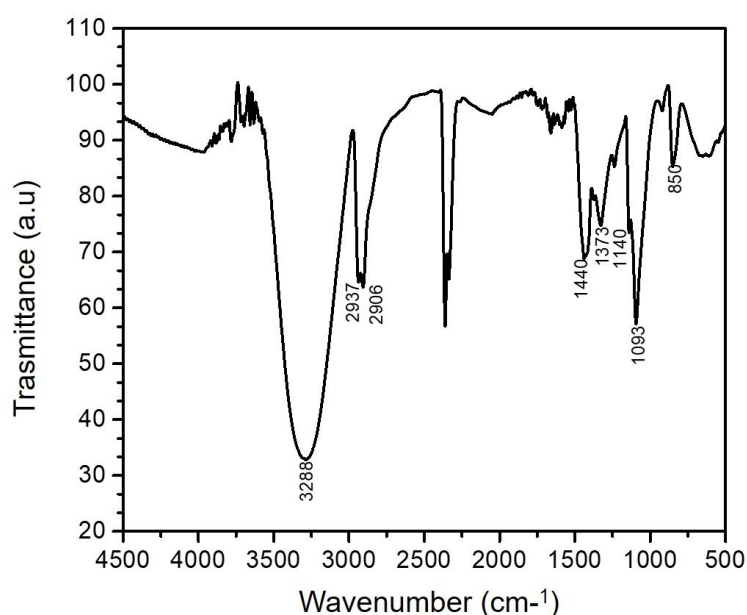


Figure 5. FTIR spectra of PVA nanofiber

Conclusion

Poly(vinyl alcohol) (PVA) at concentration of 5%, 9% and 12 w/w has been successfully spun into nanofiber. While the lowest concentration resulted in beaded fiber, increased PVA concentration to 9 and 12% resulted in beadless yet larger nanofiber. Two factors were found to influence fiber size – solution viscosity and conductivity. Curve fitting analysis showed that the influence of these two factors on fiber size perfectly fitted previous scaling law model, convincing that control of size is universal for both particle and fiber, and is highly important to predict interdependence of flowrate and conductivity on fiber diameter. The presence of hydroxyl and acetate groups were confirmed, as identified in FTIR spectrum.

Acknowledgments

This research was financially supported by Directorate of Research and Community Engagement of Ministry of Research, Technology and Higher Education, Republic of Indonesia (UNSRI) under the University's Excellent Research (PUPT) Grant in the fiscal year 2017.

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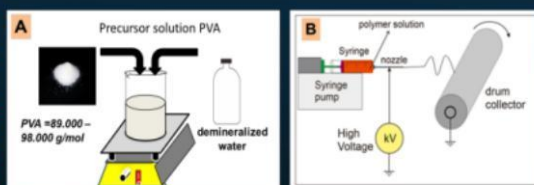


Fig 1. (a) Precursor solution and (b) Electrospinning setup

Results and Discussion

Nanofiber Morphology as a Function of Solution Properties

Figure 2 showed PVA solution at 5% w/w resulted in beaded fibers with average diameter of 287 nm and the increase in PVA concentration to 9 and 12% resulted in bead-free nanofibers with higher diameter of 328 and 440 nm, respectively. This is presumably associated with the viscoelastic jet break-up theory. In electrospinning process, viscoelastic force allows continuous and smooth elongation of the jet into fibers [1]. The elongation affects the movement of fiber towards the collector. In a less viscous solution, polymer chains are hardly entangled. As a result, when the fiber is exposed to high voltage, the poorly-entangled chains are easily extended and experience interrupted fiber thinning – the fiber strands break up and form beads [13].

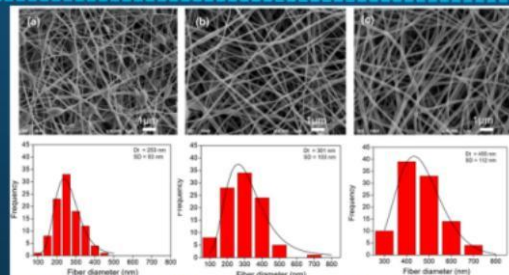


Fig 2. Morphology and size distribution of PVA nanofiber produced from PVA solution at (a) 5% w/w, (b) 9% w/w, (c) 12% w/w. Magnification 10,000x

Scaling Law Model

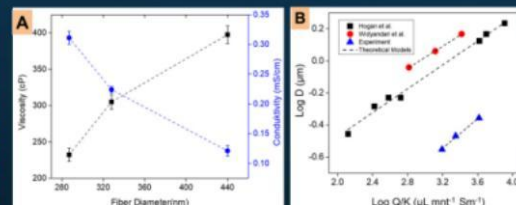


Fig 3. (a) Correlation between fiber diameter with viscosity and electrical conductivity of PVA solution and (b) Relationship between fiber diameter and flowrate-to-conductivity ratio. Upper curve: beaded fiber, lower curve: smooth fiber

Acknowledgment

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