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Research Paper

Electrospinning Growth Parameters Dependent PVP: $PC_{71}BM$ Nanofiber Structure Characterizations and Modeling

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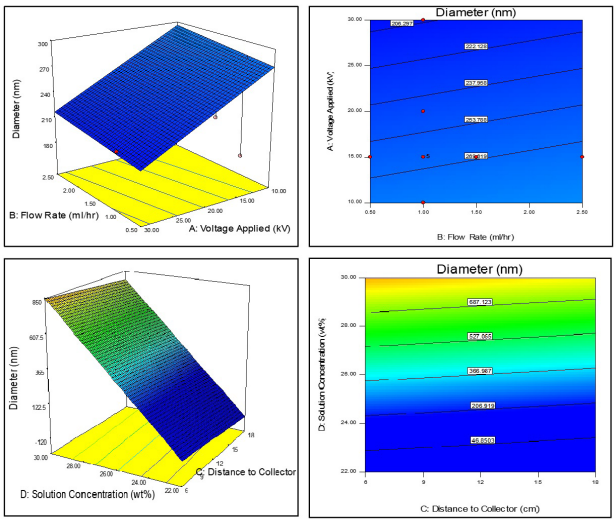
Highlights

- PVP:PC71BM nanofiber structure modeling is reported
- Applied voltage and polymer formulation weight percentage effect on nanofiber diameter is analyzed and optimized using RSM software
- Average diameter of the nano-fiber membranes decreased with increasing the applied voltage
- Average diameter of the nano-fiber increased with increasing the polymer concentration

Graphical abstract



Abstract

As green materials, the organic nano-fiber membranes are very potential for diverse functional purposes. The growth parameters based fiber alignment; surface morphology and diameter are key attentions to control mechanical, structural, electrical, and optical properties. These physical aspects of nanofiber are diversified its practical significance in which control of growth techniques is vital. Electrospinning is a facile but pragmatic approach to adjust the growth process by regulating growth parameters. In this study, fabrication of spinning parameter preference to control the nanofiber shape, diameters, and crystalline property are investigated. Different % weight of PVP and PC71BM mixture solution for electrospinning are used in this study. It is observed that the average applied field and solution concentration of active materials are paramount to well-aligned uniform diameter nanofiber having better structure and crystalline properties. The scanning electron microscopic (SEM) study of nanofiber micrograph shows the diameter size of nanofiber and it is validated by Response Surface Model (RSM). A sharp peak of polymer fiber is shown by X-ray diffraction (XRD) that realizes worthy nano-crystalline property. The overall growth process is reinforced by validation from RSM analysis.

1. Introduction

Nanofiber membranes are highly potential for diverse technological applications. As support material for electrical power generation [1], catalytic [2], antibacterial [3], and functionalized for microfiltration of water purification [4] is reported. The diverse direction of application feature is reported by Ramakrishna, S. et al., that electrospun nanofiber can solve global issues [5] Polymer energy application is widely been studied recently to investigate its prospect as an alternative to high processing cost inorganic materials. Organic semiconductors nanostructures optical absorption and rapid energy conversion are prospective. Due to high porosity and inherent large surface area to volume ratio, the electrospun nanofiber membranes are suitable for renewable energy solicitation. It is found promising nanostructure for energy harvesting [6-7] and storage purposes [8-9]. Joshi et al. report on electro span carbon nanofiber is realized suitable for a low-cost counter electrode in solar photovoltaic (SPV) [6]. The electrode arrangement in

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advance SPV is very sensitive to its performance. Nano engineering structure fabrication technique is applied to energy harvesting [10], due to its superior light coupling effect and ease fabrication process of the tiny one dimensional (1D) semiconductor nanostructures when indorsed for solar cell. It eventually achieves greater efficiency at minimum materials cost. Solution processed 1D nanostructures can easily be self-assembled [11]. In this growth feature, organic semiconductor nanostructures are one of the most prevalent nanomaterials that are used to apply in the emerging solar cell [12]. Organic solar cell-intrinsic benefits over inorganic cells have made it more attractive particularly due to its lightweight and flexibility for large scale [13], wide area [14] thin-film PV. Suitable polymer nanostructure fiber and its facile fabrication are vital for low-cost PV. Electrospun polymer-fiber solar cell developed by Nagata et al. shown promising for optical absorption at diverse polymer density [15]. Lower density red shift to dense polymer blue shift realized diverse growth strategies to develop electrospun deposited active nanofiber diverse morphology and structures. Growth and optical properties co-relation is realized in response surface methodology (RSM) significance to optimize surface quality [16]. In past study [17] and even in very recent [18], it is recognized that the fiber diameter and flexibility are critically controlled by electro-spinning parameters. The diameter, thickness, and grown polymer surface properties are supposed to be controlled by deposition voltage, flow rate, and relative weight percent (wt%) of polymer materials. Nanofiber significance in diverse applications is truly dependent on its physical properties in which control of growth technique is crucial. It is expected to be impending of nanofiber diverse physical and surface properties that feasibly control absorption level and electrical charge transfer capabilities. Therefore, diverse conditions of electrospinning parameters for PVP:PCBM polymer growth strategies of the desired surface, structural, and diameter are studied. Moreover, counter assessment of the fabricated nanofiber structural property by RSM model is proven the accuracy of approaches and standards.

2. Materials and method

2.1. Materials

Polyvinylpyrrolidone (PVP) (Mw=1,300,000) and chloroform were purchased from Sigma-Aldrich. Phenyl-C71-butyric acid methyl ester (PC71BM) (Mw=1030.93) was obtained from Luminescence Technology Corporation. All materials have been used without further purification.

2.2. Fabrication and characterization method

The solution formulation for electrospinning is made of PVP and PC71BM mixture dissolved in chloroform at concentrations of 8 mg/mL. It is then stirred at room temperature for 24-hours using magnetic stirring to allow for complete polymer dissolution. The solutions are loaded into a 10 ml glass syringe fitted with a 20 gauge Luer lock metal needle which is attached with high supply voltage. The solution is injected through the needle at a varied flow rate (0.5-2.0 mL/h) by a syringe pump (New Era Pump System, NY). A voltage of 10-25 kV is applied using a high-voltage power supply (NFIBER High Voltage, MY). The distance between the rotating collector and needle tip is varied from 5cm to20cm and the samples are collected onto a rotating collector at constant speeds of 200 rpm. The morphology of the electrospun fibers is observed using scanning electron microscopy (Hitachi S-3400N). Samples of the fiber are sectioned from the electrospinning rotating collector and are then sputter-coated with a thin layer of gold before examination in the SEM. Table 1 summarizes electrospinning parameters variation used in the preparation of PVP:PC71BM nanofiber using electrospinning technique with drum collector.

3. Result and discussions

3.1. Fabricated data analysis

Electro-spun is the utmost efficient method to produce fibers in the nanometer scale. Different diameter nano-fiber fabricated by changing the applied voltage, flow rate of solution, concentration of polymer solution, the distance between spinneret and drum, and the rotational speed of drum parameters. The relationships between the nano-fiber diameters to the applied voltage and weight % of the solution are shown in Figure 1(a)-(d) and 2 (a)-(d) respectively. The results show an increment of voltage applied will lead to decrement in the fiber diameter. The mutual relationship between the rotation speed of the collector and voltage applied was observed. The optimized electrospinning parameter to obtain the finest fiber diameter had been generated.

Figure 1(a-d) represented the SEM images of the electrospun nano-fiber membranes fabricated by the applied voltage of 10 kV, 15 kV, 20 kV, and 30 kV respectively. The average diameter of the electrospun nano-fiber with the voltage applied 10 kV, 15 kV, 20 kV, and 30 kV are 275±0.1 nm, 220±0.4 nm, 222±0.2 nm, and 208±0.3 nm respectively. Based on the result of SEM images, it is found that the average diameter of the electrospun nano-fiber membranes is decreased by increasing the applied voltage. However, at 30 kV applied voltage, relatively poor quality fiber with beads was observed that might be attributed to the high wt% in the solution that induced formation of which depends on the net charge repulsion and the interaction of the net charge with the electric field [19].

From the concentration-dependent SEM image, it is realized that droplet of polymer for low solution concentration while uniform electrospun fiber is formed when the solution concentration is 30 wt%. At low concentration, there is less polymer content in the electrospinning solution hence, electrospray occurred instead of electrospinning. However, in high solution concentration, the high polymer content in the electrospinning jet caused polymer chains to have more interactions that resulted in uniform and large size of electrospun fiber [20].

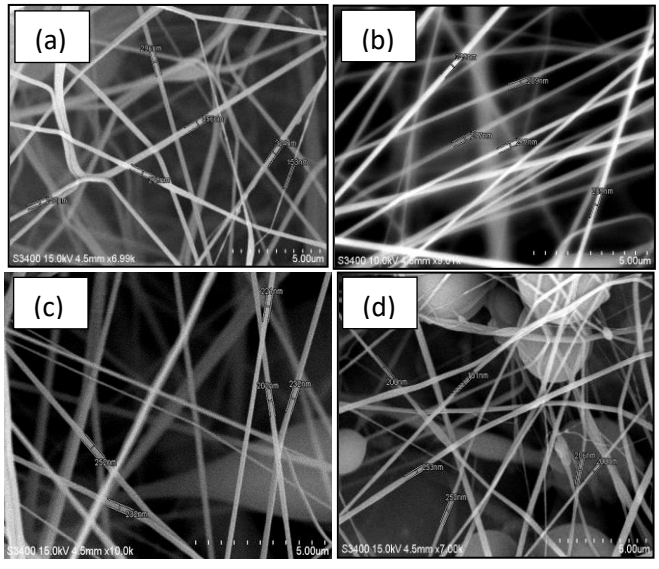

Fig. 1. SEM image of the fiber fabricated with different voltage applied (a) 10kV, (b) 15kV, (c) 20kV, and (d) 30kV.

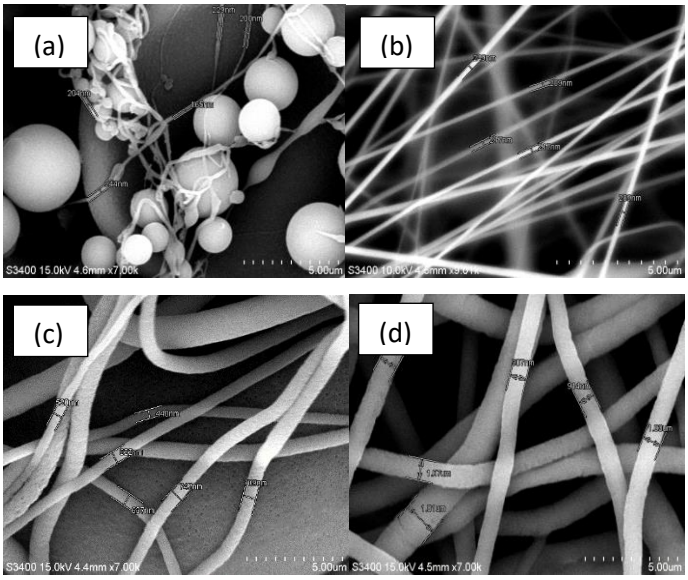

Fig. 2. Polymer concentration dependent SEM image for (a) 22 wt%, (b) 25 wt%, (c) 28 wt%, and (d) 30 wt%.

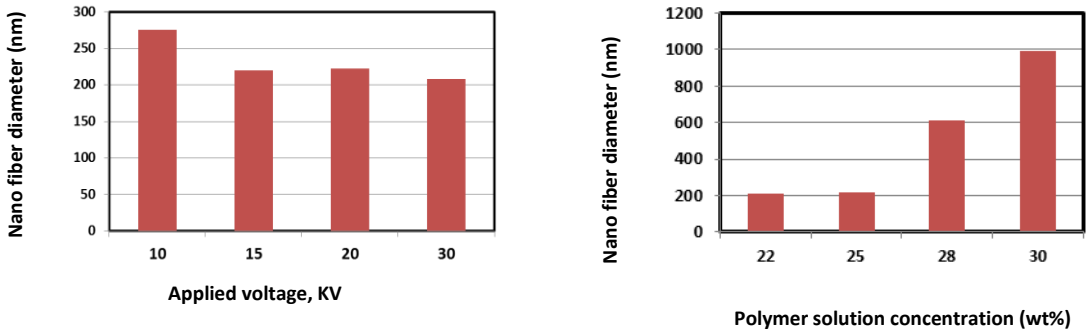

Fig. 3. Average diameter of fiber against applied voltage (a); solution concentration (b).

Table 1
Summary of the Effect of Electrospinning Parameter of PVP: $PC_{71}BM$.

Electrospinning Parameters	Parameter Change	Diameter Change	Observation
Voltage Applied	Increase	Decrease	Formation of bead when the voltage was too high.
Flow Rate	Increase	Increase	Formation of bead when flow rate is too low. Flattened web fiber obtained when the flow rate is too high.
Distance between Spinneret to Collector	Increase	Decrease	Formation of bead when the distance to collector is too short.
Solution Concentration	Increase	Increase	Electrospray occur when the solution concentration is too low. Micro-scale fiber was obtained as the solution concentration was high.
Rotation Speed of Collector	Increase	Decrease	Straight and uniform alignment fiber obtained at high rotation speed of collector.

In Figure 3(a), the average nanofiber diameter of each SEM picture is shown by a bar graph focusing on the size distribution. The fiber diameter is reduced with increasing applied voltage. This is due to the increasing applied voltage cumulative electrostatic force that may act on the electrospinning solution. An increase in applied voltage, create higher electrical force on the needle tip and induce greater stretching and pulling effect on the jet solution [21]. The greater electrostatic force has shown to overcome the surface tension of the solution and enable the solution to stretch more, resulting in a smaller diameter of the electrospun fiber. Resulted in Figure 3(b), the diameter of the electrospun fiber increased from 208 nm to 990 nm (approximately) when the solution concentration is increased from 22 wt% to 30 wt%. The solution concentration resulted in being the most significant effect on the fiber diameter compared to the other parameters. This is possibly due to the increases in the viscosity of the electrospinning solution at greater solution concentration. It may enhance the electrostatic force that is needed to stretch the fiber. Thus, a greater diameter of the electrospun fiber is achieved as the fiber experiences inadequate stretching due to the higher concentration and viscosity of solutions.

Table 1 shows the variability and trends of the parameters of nanofiber diameter change.

Based on the summary in Table 1, the increase in applied voltage causing the fiber diameter becomes thinner. The flow rate of the solution resulted that the greater diameter of fiber membranes was fabricated at a higher flow rate. For low concentration solution droplet formation in the fiber is observed. High solution concentration relatively greater diameter fiber that is beyond nano-scale is found. Therefore, it is important to discover the parameter that able to fabricated finer fiber diameter while free from droplet formation. Based on the result 25 wt% solution concentration and 15 KV applied voltage are considered the best parameter setting in our study.

3.2. Response Surface Model

Effect of the electrospinning parameters such as voltage applied, solution concentration, and speed of rotation faction are investigated to control the morphologies of the PES fiber membranes. To minimize the diameter of the PVP-PCBM fiber membranes the optimized growth parameters are set and real processing data after fabrication are examined by using SEM and XRD.

The optimized electrospinning parameters are counter assessed by using Response Surface Methodology (RSM) simulation. The collected experimental data are inserted into the response surface methodology model by using the Box-Behnken design. The relationship between each of the parameters is verified. Besides, the optimized electrospinning parameters for the minimized diameter of the fiber is obtained. 3D response surface plot shown in Figure 4 and 5 are generated for the data corresponding to Figure 1 and 2 results. The relationship between the fiber diameters to the voltage applied and weight % of solution weight are investigated using RSM. The solution concentration increased, the distance between spinneret to collector need to be increased to maintain the fiber diameter. The software data shows well consistent with the experimental data. Based on the surface morphology, 15kV and 25 wt% are the best parameter setting in all respect.

3.3. X-Ray diffraction result

XRD analysis for the PVP:PCBM concentration ratio (3:1) of fiber membranes was performed. By applying the Scherer Equation, the polymer nano-crystalline pattern resulted in data shown in Figure 6.

From the XRD spectrum shown in Figure 6, the 2Θ=65.27° with FWHM=0.32°. From the data, the calculated nano-crystalline fiber size, d = 294.7 nm. However, the average fiber diameter from the SEM image in Figure 1 and the fiber size calculated from RSM has confirmed the growth and characterization process accuracy. Hence, the XRD sharp and intense peak with nano-crystalline property is realized.

4. Conclusion

Organic nanofiber membrane growth parameters based fiber diameter and surface morphology are investigated. Applied voltage and solution concentration influence on nanofiber diameter is analyzed. The mechanism of nanofiber physical structure by controlling the growth technique is understood. Electrospun nanofiber with the application of 10 kV, 15 kV, 20 kV, and 30 kV voltage, the average diameter is 275 nm, 220 nm, 222 nm, and 208 nm respectively. The resulted diameter of the electrospun fiber is increased from 208 nm to 990 nm while the solution concentration increased from 22 wt% to 30 wt%. The average applied field (voltage) and solution concentration of active materials are revealed best for well-aligned, uniform diameters nanofiber with good surface and structural properties. From SEM image nanofiber diameter is measured and Response Surface Model (RSM) validation revealed our methodological perfection to control the surface and diameter allied structural properties by electrospinning parameters setting. It is very potential for the purposeful application of the nanofiber membrane.

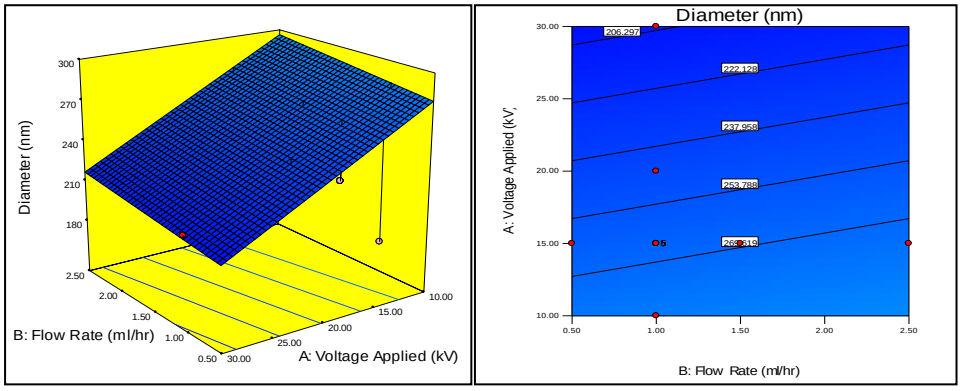

Fig. 4. 3D surface plot of diameter of fiber to voltage applied and flow rate(a); contour plot of diameter of fiber to voltage applied and flow rate (b).

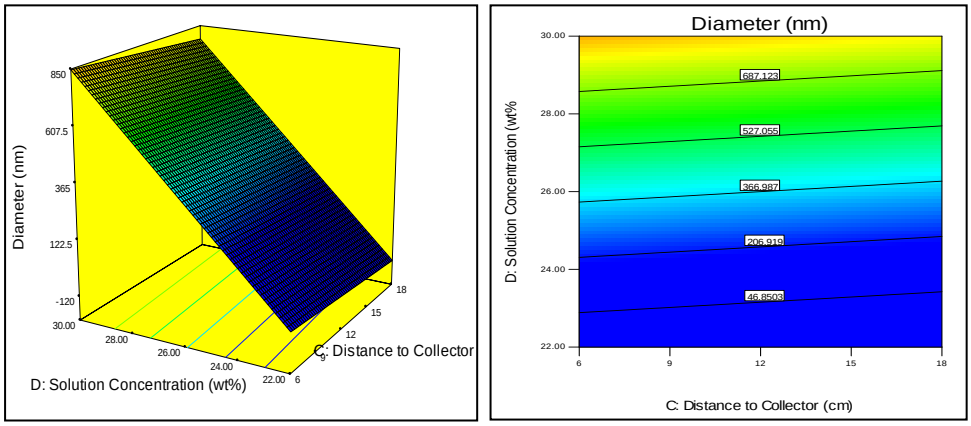

Fig. 5. 3D Surface Plot of Diameter of Fiber to Distance to Collector and solution concentration (a); contour plot of diameter of fiber to distance to dollector and solution concentration (b).

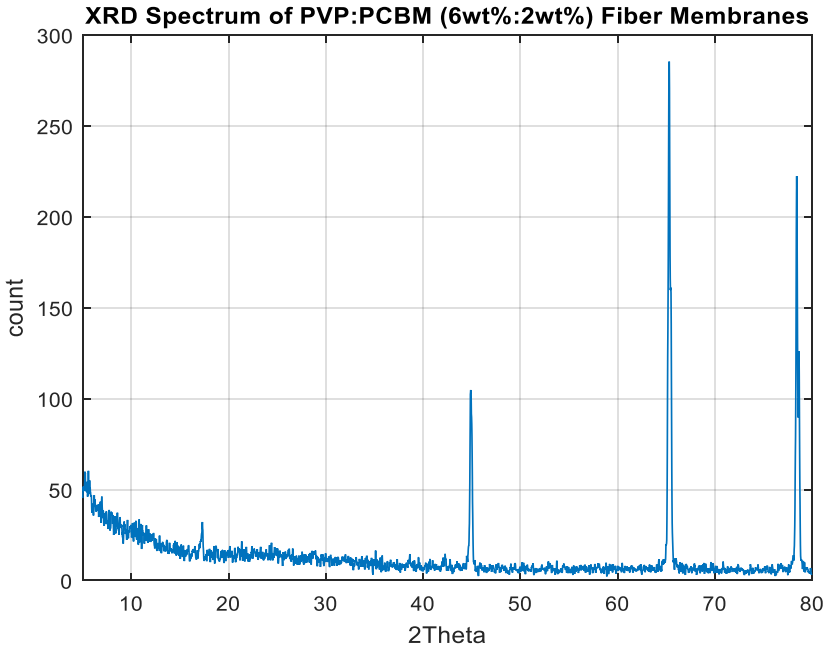

Fig. 6. XRD spectrum of PVP:PCBM concentration ratio (3:1) %wt of fiber membranes.

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Abbreviations

PVP	Polyvinylpyrrolidone
PC71BM	Phenyl-C71-butyric acid methyl ester
RSM	Response Surface Model
XRD	X-ray diffraction
SPV	Solar photovoltaic

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