Synthesis and characterization of electrospun fiber chitosan/polyvinyl alcohol/polyvinylpyrrolidone

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Abstract. Synthesis and characterization of electrospun fiber chitosan/polyvinyl alcohol/polyvinylpyrrolidone have been studied. Electrospun fiber is a fiber produced from the electrospinning process that utilizes the power of electricity to produce polymer fibers with nano to micro diameters. The purpose of this study is to synthesize and characterize electrospun fiber from chitosan/polyvinyl alcohol/polyvinylpyrrolidone. The mixture of chitosan/polyvinyl alcohol/polyvinylpyrrolidone solution is placed in an electrospinning capillary with a diameter of 0.57 mm with an electrospinning voltage of 25 kV and a distance between the tip of the spinneret and the collector by 10 cm. The resulting electrospun fiber is analyzed with fourier transformed infrared spectroscopy and scanning electron microscopy. Based on the FTIR spectra, it was found that the electrospun fiber produced consisted of chitosan, polyvinyl alcohol and polyvinylpyrrolidone. SEM analysis results show that the electrospun fiber obtained has an average diameter of 93.1 - 168.7 nm.

1. Introduction

Electrospinning is a technology commonly used for electrostatic formation of fibers that utilizes the power of electricity to produce polymer fibers with nano to several micro-sized diameters using polymer solutions both natural and synthetic polymers. The electrospinning process can be used to produce fibers in the submicron range, which are difficult to synthesize using conventional mechanical fiber spinning methods [1]. Electrospun fibers from a polymer material are made and examined because they have specific properties such as a large surface, small pore size, and the possibility to form three-dimensional structures. In its application in the biomedical field it can be used as a wound dressing material [2]. One of the biomaterials that can be used to make electrospun fibers is chitosan [3]. Based on the nature of chitosan as an antimicrobial, biocompatibility and high biodegradability, as well as wound dressing, this material is widely used in the medical field [4,5]. In order to be used in the medical field, electrospun must be compatible with cell tissue. Polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) are examples of the tissue compatible compounds. PVA is a hydrophilic, biodegradable and biocompatible synthetic polymer that has been widely used in the biomedical field and it is also an excellent material for making fiber [6]. This material is benign to living tissues, harmless, and nontoxic [7]. PVP is a synthetic polymer that has good biocompatibility properties and has long been applied as a biomaterial or additive to drugs [8]. Because of the various advantages
and the specific benefits associated with electrospinning, PVP is widely used in making fiber through electrospinning with various materials which cannot be modified by acting as a polymer carrier [9].

For providing the desirable polymeric materials with combined properties for particular applications, can be done by blending several polymers. Recently, blends of natural polymers have been becoming considerably important due to their strong potential in replacing synthetic polymers in many applications. The concentration of PVA, voltage electrospinning, and concentration of PVP are important parameters that affect the morphology and the average diameter of electrospun fiber [6]. In this research, the effect of mixture composition chitosan/PVA/PVP were investigated and characterized by Fourier Transform (FT-IR) spectroscopy and SEM (scanning electron microscope).

2. Method

The tools used in this study include Pyrex glass equipment, analytical balance Sartorius, thermometer, magnetic stirrer, electrospinner:Nabond Nano E-Spinning Unit, FTIR (Perkin Elmer Spectrum), SEM (JSM-6510LA). The materials used in this study include chitosan: from CV. ChiMultiguna, DD 95.88% pharmaceutical grade, PVA p.a from Sigma-Aldrich, PVP (Nanhang Industrial Co., LTD., K-30 pharmaceutical grade), CH₃COOH (Merck, pro analysis). Chitosan/PVA/PVP making and mixing using the method from Ma et.al [10]. Chitosan is dissolved in acetic acid (aq) (1%) 40 mL to a homogeneous solution with a concentration of 1 wt%, PVA powder was dissolved in distilled water with magnetic stirrer for 6 hours at 120°C then allowed to stand at room temperature to form a homogeneous solution with a concentration of 5 wt%. PVP powder was dissolved in distilled water with a magnetic stirrer stirrer until a weight of 10 wt% was reached, in a homogeneous solution. Then the solution of chitosan, PVA and PVP is mixed with the composition variations. The mixture of chitosan/PVA/PVP solution is then placed in an electrospinning capillary with a diameter of 0.57 mm with an electrospinning voltage of 25 kV, and distance between the tip of the spinneret and the collector by 10 cm. The syringe is pressed with nitrogen gas pressure to drive the booster so that during the experiment the conditions of making the fiber are practically stable at the range of the DC voltage used. Electrospun fiber that has been synthesized is then characterized by using FT-IR and SEM.

3. Results and Discussion

3.1. Synthesis of electrospun fiber chitosan/PVA/PVP

In this research, synthesis of chitosan/PVA/PVP fiber electrospun was carried in the various composition. The results obtained show that the electrospun fiber is white with a circle membrane pattern and evenly distributed. The differences in the results of chitosan/PVA/PVP fiber electrospun synthesis using Nabond Nano E-Spinning Unit electrospinning can be seen in the number of beads or lumps in the electrospun fiber which can be seen in the Table 1 and Table 2. The electrospinning results in the PVA/PVP mixture with the addition of chitosan solution in Table 1, showed that electrospun fiber samples C and D have the most wet fibers or beads seen at the bottom of the membrane, this can occur because the distance is still too close so that the solution that has not been evaporated sticks to the collector [11]. Besides the addition of chitosan can also increase the boiling point so that the polymer solution will be more difficult to evaporate.

| Sample | Number of Beads | Explanation |
|--------|-----------------|-------------|
| A      | 82              | Less        |
| B      | 108             | Less        |
| C      | 182             | Middle      |
| D      | 248             | More        |

Table 1. The number of beads on electrospun chitosan/PVA-PVP fibers variants
Table 2. The number of beads on electrospun PVP/PVA-chitosan varians

| Sample | Number of Beads | Explanation |
|--------|----------------|-------------|
| E      | 262            | More        |
| F      | 253            | More        |
| G      | 193            | Middle      |
| H      | 120            | Less        |

The electrospinning results in the PVA/chitosan mixture with the addition of PVP in Table 2, showed that electrospun fiber samples E and F contained the most wet fibers or beads seen at the bottom of the membrane, this can occur because the distance is still too close so that the solution that has not been evaporated sticks to the collector [11]. Addition of PVP can cause the boiling point of the polymer solution to decrease so that the G and H samples of the wet fibers or beads produced are less.

3.2. Functional group analysis with FT-IR

FT-IR characterization was carried out to determine the functional groups in electrospun fiber. The results obtained are then compared with a variety of FT-IR spectra in order to know the difference in the functional groups of each electrospun fiber material. The results of FT-IR spectra analysis in Figure 1a show that chitosan/PVA membranes have absorption on certain waves, namely in a very strong strain centered at 3401 cm\(^{-1}\) which is characteristic of -OH from chitosan and PVA, weak strain at 2929 cm\(^{-1}\) originates of -CH in chitosan and PVA, the absorption valley at 1651 cm\(^{-1}\), 1570 cm\(^{-1}\), 1435 cm\(^{-1}\) originating from C = O, N-H and C – H contained in chitosan, asymmetrical strain at 1099 cm\(^{-1}\) and 919 cm\(^{-1}\) is the C-O uptake area of chitosan and PVA, the valley at 851 cm\(^{-1}\) is the C-C uptake area of PVA.

The results of FT-IR spectra analysis in Figure 1b show that PVA/PVP membranes have absorption at certain waves, that is, at very strong strain centered at 3564 cm\(^{-1}\) is the –OH characteristic of PVA, the valley at 1658 cm\(^{-1}\) originates from C = O contained in PVP and 1461 cm\(^{-1}\) originates from C – H found in PVP and PVA, asymmetrical strain at 1141 cm\(^{-1}\) and 920 cm\(^{-1}\) is the C-O absorption area of PVA, the valley at 856 cm\(^{-1}\) is C-C absorption area of PVA.

The results of FT-IR spectra analysis in Figure 1c show that chitosan/PVA/PVP membranes have absorption at certain waves, that is, at very strong strain centered at 3402 cm\(^{-1}\) is characteristic –OH from chitosan and PVA, weak strain at 2929 cm\(^{-1}\) originates from –CH in chitosan and PVA, valleys in 1651 cm\(^{-1}\) are characteristic of C = O from chitosan and PVP, 1436 cm\(^{-1}\) originates from C – H found in chitosan, PVP and PVA, valley 1293 cm\(^{-1}\) originates from C-N in PVP, asymmetric strain at 1095 cm\(^{-1}\) and 919 cm\(^{-1}\) is the C-O absorption area of chitosan and PVA, the valley at 851 cm\(^{-1}\) is the C-C absorption area of PVA. Comparison of FT-IR spectra of chitosan / PVA, PVA / PVP, and chitosan/PVA/PVP can be seen in Table 3.
Figure 1. FT-IR spectra of (a) chitosan/PVA (b) PVA/PVP (c) chitosan/PVA/PVP

Table 3. Comparison of FT-IR spectra of chitosan [12], PVA [13], PVP [14] with chitosan/PVA, PVA/PVP and chitosan/PVA/PVP research result

| Functional groups | Chitosan | PVA | PVP | Chitosan/PVA | PVA/PVP | Chitosan/PVA/PVP |
|-------------------|----------|-----|-----|--------------|---------|-----------------|
| O–H               | 3379     | 3247| 3434| 3401         | 3564    | 3402            |
| C–H               | 2879, 1421| 2914| 2955, 1424| 2929, 1435| 1461    | 2929, 1436      |
| C=O               | 1644     | -   | 1661| 1651         | 1658    | 1651            |
| N–H               | 1596     | -   | -   | 1570         | -       | -               |
| C–O               | 1083     | 1082, 1414| -   | 1099, 919   | 1141, 920| 1095, 919       |
| C–N               | 1379, 1320| -   | 1291, 1081| -           | -       | 1293            |
| C–C               | -        | 851 | -   | 851          | 856     | 851             |

3.3. Morphological analysis with scanning electron microscopy (SEM)

The analysis results using SEM of electrospun PVA/PVP are presented in Figure 2 and Figure 3. Characterization using scanning electron microscopy (SEM) was carried out to determine the surface morphology and diameter of the chitosan/PVA/PVP fiber electrospun produced. The parameters that make optimal or not the results of making electrospun fiber seen from the uniformity of the fiber and the smaller diameter. SEM results obtained in Figure 2 and Figure 3 show that the fibers are evenly distributed and sustained and there are many cross-bonds that occur, but the results obtained are still found many clots or beads. This is likely to occur because at the preparation stage, the mixture of chitosan, PVA and PVP polymers is not completely dispersed, causing the solution to become inhomogeneous. Inhomogeneous solutions can cause beads [15].
Figure 2. Photograph morphology of electrospun PVA/PVP fiber with the addition of chitosan solution (a) 0 mL (b) 1 mL (c) 2 mL (d) 3 mL.

Figure 3. Photograph morphology of electrospun PVA/chitosan fiber with the addition of PVP solution (a) 0 mL (b) 1 mL (c) 2 mL (d) 3 mL.

The appearance of lumps or beads can also be caused by the flow rate that is too fast [16]. The flow rate that is too fast affects the increase in the amount of electrospinning solution that flows through the tip of the spinneret, so that it will cause instability taylor cone, taylor cone that is formed will quickly fall into the collector and there is not enough time for the electrospinning solution to evaporate, which will cause the formation of beads.
To find out the distribution of electrospun fiber at each concentration of chitosan, PVA and PVP, fiber diameter measurements were performed using ImageJ software. The composition of the electrospun fiber is measured randomly by marking 50 different points so that the uniformity and differences in the fiber diameter produced at various concentrations of chitosan, PVA and PVP are used. The measurement results can be seen in Figure 4.

![Figure 4](image-url)

**Figure 4.** The average diameter of electrospun fiber (a) PVA-PVP to the addition of chitosan (b) PVA-chitosan to the addition of a PVP solution

The results obtained indicate that the more chitosan solution added to the PVA-PVP polymer mixture will produce a smaller diameter of the fiber, this is in accordance with the previous research that the addition of chitosan can reduce the diameter of the fiber produced [5], because chitosan is a linear cationic polymer, so chitosan will increase the conductivity of the solution and thus reduce the diameter of the fiber. Whereas the electrospun PVA-chitosan fiber with the addition of PVP shows that more PVP added to the PVA-chitosan polymer mixture will produce a larger diameter. This is consistent with result of the previous research that the average diameter of the fiber produced increases with increasing PVP concentrations used [17]. The increase in the average diameter of the fibers produced is in line with the increasing concentration of PVP used, because the more PVP added to the electrospinning solution will further increase the viscosity of the solution so that the fiber produced in the electrospinning process will be even greater[18].

4. **Conclusion**

The results showed that electrospun fiber obtained had an average diameter of 93.1 - 168.7 nm. The concentration of chitosan and PVP used affects the diameter of the fiber produced. Based on the FT-IR test, it was found that the electrospun fiber produced consisted of three components namely chitosan, PVA and PVP.

5. **Acknowledgements**

This research was supported by The Center for Nuclear Fuel Technology (PTBBN) - BATAN which provided the electrospinner as the main research instrument.

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