Electrospinning of nanofibers chitosan/PVA-sodium silicate

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Abstract. Chitosan is one of the biomaterials used in making membranes using electrospinning techniques. Chitosan was chosen because it has high biocompatibility and biodegradability. Chitosan solution has high viscosity even at low concentrations therefore this polymer is very difficult to be electrospinned without other polymers addition. Mixing polymer solution is a method commonly used to provide the desired polymer solution material with combined properties for certain applications. Polyvinyl alcohol is an excellent material for making fiber. In making membranes using solvent evaporation techniques, sodium silicate added to the chitosan solution will make the chitosan-silica membrane become porous even though the effect is not significant. This article will discuss the effect of adding sodium silicate to the manufacture of chitosan-PVA-sodium silicate membranes using electrospinning method. The results showed that sodium silicate solution addition to CS/PVA polymer solutions increases the fiber diameter percentage to be <100 nm and increased the fiber uniformity, especially in chitosan/PVA polymer mixtures with volume ratio of 2:8. The addition of sodium silicate solution to the chitosan/PVA polymer solution reduces the CS/PVA-sodium silicate fibers thermal stability but increases the CS/PVA-sodium silicate fibers hydrophilicity.

1. Introduction

The main principle of the electrospinning process in producing fiber electrospun is done in two ways simultaneously, that is material solution spraying and stretching results spraying by the electron field between the two electrical terminals. The conductive solution in the syringe is pushed continuously by the drive system so that it can come out through a needle that has been connected with positive electrode. At first the solution will form a straight line and will turn to be unstable due to electric field of the high-voltage power supply. The formed fiber structure will be piled up on the collector plate connected to the negative electrode [1-2].

Generally, there are two general parameters in regulating fibers of the electrospinning process, they are solution intrinsic properties (such as viscosity, electrical conductivity, polarity and surface tension) and operational conditions (such as potential difference, the distance between collector and spinneret and the flow rate of solution). Moreover, environmental temperature and humidity factors can also affect the electrospun fiber form [3]. The electrospinning process must use solution that has high enough viscosity and the material that is conductive. The choice of polymer to be mixed with chitosan depends on the properties that will be improved.

Chitosan [poly(2-amino-2-deoxy-D-glucose)] is the second abundant natural polymer after cellulose. Chitosan is non-toxic, biodegradable, biocompatible and anti-bacterial. Chitosan is a derivative of chitin [1-4-linked 2-acetamido-2-deoxy-β-D glucopyranose [4-6]. Polyvinyl alcohol (PVA) with the chemical formula [(C₂H₄OH)x] is a synthetic polymer produced by hydrolysis of...
polyvinyl acetate. It is non-toxic and soluble in water, so it is widely used in various fields, including medical and pharmaceutical fields. Polyvinyl alcohol (PVA) has hydrophilic properties so it is selective about water. This hydrophilic nature is caused by the –OH group interacting with water molecules through hydrogen bonds. As a result, this PVA membrane has swelling properties if there is water from the feed to be separated, PVA can be dissolved in water with the heat help at temperatures above 90°C. At room temperature PVA is solid, has molecular weight of 85.000-146.000, has glass transition temperature (Tg) of 228-256 °C. Polyvinyl alcohol (PVA) is very well used to form films, emulsifying and adhesive properties, resistant to oils, fats and solvents, odorless, non-toxic and has high tensile strength [7-8].

Chitosan solution mixture which has low deacetylation degree with PVA to get solution with high viscosity was used by [7]. The resulting membrane has low thermal stability, high mechanical properties and is stable in acidic and basic media. The membrane has high absorption on methyl orange, Fe(III) and Cr(VI) ions. The hydrophilic nature of chitosan is modified with mixture of polymers such as polyethylene glycol (PEG), polyethylene oxide (PEO) and poly vinyl alcohol (PVA). A mixture of chitosan and PVA was used by [9] as membrane-making material by electrospinning method. Diameter of the obtained membrane ranges from 50-130 nm. The resulting membrane is claimed to be separating membrane. The material mixture of chitosan, PVA and gelatin was used by [4] as porous membranes making material with electrospinning method. The optimum material weight ratio (2:2:4) produces membrane with diameter of 150 nm. The cross-linked membranes using glutaraldehyde produce higher mechanical properties than non-cross-linked membranes. Carboxymethyl chitosan cross-linked alginate dialdehyde as a membrane composite material was used by [10]. The addition of polyethylene oxide (PEO) is an important material as a composite forming media in the membranes manufacture using electrospinning reactive methods.

Chitosan/PEO/silica nanofibers, TEOS and GPTEOS combination were used as silica precursors. A 50/50 wt % CS(PEO)/SiO$_2$ ratio produces fiber with average diameter of 182±16 nm and compact structure [4]. Tetraethyl orthosilicate (TEOS) was used as silica source and polyvinylpirolidone (PVP) as silanol group carriers and butanol as solvents during the electrospinning process. The calcination process on TEOS was carried out at various temperatures, such as 500°C, 700°C and 1000°C. The results shows that the calination process at 1000°C causes nanofiber silica crystallinity increases but silanol bond of the group (Si-O-Si) is shrinking [7].

Sodium silicate isolated from rice husk ash as silica source to synthesize chitosan-silica membranes with solvent evaporation techniques was used by [11]. The solvent evaporation technique is one of membrane synthesis techniques by solvent evaporation using room temperature. The results show that the characterization using FTIR and NMR indicates hydrogen bonding occurs between chitosan and SiO$_2$. The thermal and mechanical stability is higher compared to chitosan alone, but the increase in silica does not significantly increase the pore in the produced chitosan-silica membrane. The characteristics of chitosan-silica membrane cause the minimal use of the membrane as separating membrane. The membrane function tends to be as adsorption membrane that relies on the -NH$_2$ active group on chitosan. According to literature research, chitosan and chitosan silica membranes synthesis using the electrospinning method can produce porous membranes that have opportunities as separating membranes, anti-bacterial membranes, and adsorption membranes. This article discusses the effect of sodium silicate solution addition to chitosan/PVA polymer solution on the characteristics of the produced chitosan/PVA-silicate electrospun nano fibers membrane.

2. Methods

Chitosan/PVA-sodium silicate membrane synthesis using electrospinning method. For Preparation of 4 wt% chitosan solution, as 4 grams of chitosan was dissolved in 100 mL acetic acid (40%) then stirred with magnetic until the solution was homogeneous. Preparation of 20 wt% PVA solution, 20 grams of PVA powder was dissolved in distilled water with magnetic stirrer for 2 hours at 85°C then left to stand at room temperature homogeneous solution was formed [12], 4% of chitosan solution and
20% PVA solution were mixed with various volume variations and added with sodium silicate solution as shown in Table 1.

| Sample | Chitosan 4% (mL) | PVA 20% (mL) | Sodium silicate (mL) |
|--------|------------------|--------------|---------------------|
| A      | 2                | 8            | 0.16                |
| B      | 4                | 6            | 0.16                |
| C      | 5                | 5            | 0.16                |
| D      | 6                | 4            | 0.16                |
| E      | 8                | 2            | 0.16                |
| F      | 2                | 8            | 0.32                |
| G      | 4                | 6            | 0.32                |
| H      | 5                | 5            | 0.32                |
| I      | 6                | 4            | 0.32                |
| J      | 8                | 2            | 0.32                |

The polymer/PVA-sodium silicate solution is then put into electrospinning capillary with diameter of 0.57 mm with electrospinning voltage of 17 kV and distance between the tip of spinneret and the collector as much as 15 cm. The syringe is pressed with nitrogen gas pressure to drive the booster with flow velocity of 0.3 mL/hr. Characterization of chitosan/PVA-sodium silicate membrane: Surface morphology and cross-sectional test on membranes using Scanning Electron Microscope (SEM). Function group test on membranes based on qualitative test results using Fourier Transform Infrared (FTIR) spectrophotometers. Thermal stability test on membrane using Thermogravimetric Analysis (TGA) method. Swelling Index Measurement (SI): membranes with certain weight were immersed in 10 mL in various buffer solution medium that is 4.0-11.0 for 24 hours and then SI value is calculated using the following formula,

\[
\text{SI} (%) = \frac{W_w - W_d}{W_d} \times 100
\]

Note: \(W_w\) = weight after immersion, \(W_d\) = initial weight [13]

3. Result and Discussion

The results of SEM chitosan/PVA-sodium silicate fiber electrospun and electrospun fiber morphological analysis are done by calculating the SEM fiber results diameter at several points using ImageJ software [14] presented in Figure 1-5.

The addition of sodium silicate solution to chitosan/PVA polymer solution increases fiber diameter percentage of (<100 nm) and increases fiber uniformity, mainly in chitosan/PVA polymer mixture with volume ratio of 2:8, whereas in chitosan/PVA polymer solution composition with increase in the amount of chitosan (decrease in the amount of PVA) tends to reduce the percentage of fiber diameter and reduce fiber uniformity. An increase in chitosan concentration (decrease in PVA concentration) causes the polymer solution to move quickly leaving the syringe. Very high flow rate causes the fiber beads to form and the resulting nano fibers will become rough and not smooth.
Figure 1. SEM photos of nanofibers

Information Figure 1:
1. SEM photo of nanofiber sample A
2. SEM photo of nanofiber sample B
3. SEM photo of nanofiber sample C
4. SEM photo of nanofiber sample D
5. SEM photo of nanofiber sample E
6. SEM photo of nanofiber sample F
7. SEM photo of nanofiber sample G
8. SEM photo of nanofiber sample H
9. SEM photo of nanofiber sample I
10. SEM photo of nanofiber sample J

Beads are usually considered to be poor quality fiber (fiber defect) characterized by spots/granules on nano fibers. In Figure 1.(e) and Figure 1.(j) SEM photo with chitosan/PVA 8:2 composition it is the
worst quality fiber result so that the fiber percentage with diameter <100 nm cannot be calculated. The membrane that occurs is likely to be in the form of a spot membrane, the collected fibers condition concentrated only in one point, therefore that fiber only thickens on the middle side.

It is in accordance with the research of [12], nanofiber diameter increases with the silica addition from 0 to 40 wt %. The increase in the nanofiber diameter is caused by an increase in the thiol-silica addition to the polymer solution. The movement of polymer chains is inhibited by the bonding among electrons on the silica surface and the –OH or –COOH groups of the polymer solution. According to [15] the increase in PVA amount contained in a polymer solution with the same amount of TMOS (tetra methyl ortho silicate) causes the fiber diameter to decrease due to the polymer solution viscosity with PVA/TMOS volume ratio of 3:4 with the highest quality and the best fiber quality. Generally, it is said that the polymer solution viscosity increases along with the increasing of PVA concentration in polymer solution. In line with the study results of [16], the increase in PVA concentration in PVA/SiO$_2$ resulted in increase in uniformity in fiber morphology produced. Concentration of 8% PVA solution is the optimal concentration to prepare PVA/SiO$_2$ fiber. The same thing was also stated by [13] in the fiber formed from chitosan/PVA 2:1 comparison in the beads form. Chitosan/PVA comparison with ratio of 1:1 can form fiber that is beads free with fiber diameter <100 nm. The morphology of produced fiber depends on PVA content in polymer solution. As the PVA content increases the more homogeneous and uniform the fiber produced is, and vice versa the more increasing of chitosan content the resulting fiber morphology is found to be increasingly beads shaped.

Tests for functional group changes were carried out using FTIR spectroscopy. The results of FTIR spectra are presented in Figure 2.

The results of FT-IR spectra analysis in Figure 2 show that chitosan/PVA membrane has absorption on certain waves, that is in a very strong strain centered at 3401 cm$^{-1}$ which is characteristic of –OH from chitosan and PVA, the absorption valley at 1651 cm$^{-1}$, 1570 cm$^{-1}$, 1435 cm$^{-1}$ originating from –CH in chitosan and PVA, valleys at 1099 cm$^{-1}$ and 919 cm$^{-1}$ is the C–O uptake area from chitosan and PVA, the valley at 851 cm$^{-1}$ is the C–C uptake area from PVA.

The results obtained are combination of chitosan and PVA spectra that have been done by [6, 16]. The results of FT-IR spectra analysis shows that the chitosan/PVA membrane has absorption on certain waves, that is in a very strong strain centered at 3402 cm$^{-1}$ is the –OH characteristic from chitosan and PVA, the weak strain at 2929 cm$^{-1}$ originates from –CH in chitosan and PVA, valleys at 1651 cm$^{-1}$ are the C=O characteristics from chitosan, 1436 cm$^{-1}$ originating from –C–H contained in chitosan, asymmetrical strain at 1095 cm$^{-1}$ and 919 cm$^{-1}$ are uptake regions C–O from chitosan and PVA, the valley at 851 cm$^{-1}$ is the C–C uptake area from PVA. In general, the results of infrared spectra, the addition of sodium silicate solution to the chitosan/PVA polymer solution shows increase in the –OH group absorption at wave numbers around 1080 cm$^{-1}$. It is due to the –OH group from chitosan, PVA and sodium silicate addition. The shifting absorption of –OH group towards smaller wave numbers on the membrane indicates the interaction between the –OH group on PVA and sodium silicate with –NH on chitosan (although it is not significant).

The results of chitosan/PVA-sodium silicate TGA test in various compositions are presented in Figure 3. The increase in PVA content in the chitosan/PVA polymer solution decreases the thermal stability of the resulting fiber. And vice versa the more increasing of chitosan concentration in chitosan/PVA polymer solution, it increases thermal stability of the resulting fiber. It is due to the reduced number of hydrogen bonds between chitosan and PVA. The addition of sodium silicate solution also does not increase thermal stability. It is possible to happen because sodium silicate addition is too small compared to chitosan or PVA amount in polymer solution. In the chitosan/PVA-sodium silicate polymer solution with volume ratio of 2:8:0.32, weight ratio calculation (1:20:5) is obtained.
Figure 2. FTIR spectra of sodium silicate (a), PVA (b), chitosan (c), (d) nanofiber of chitosan/PVA 2:8, (e) nanofiber of chitosan/PVA-sodium silicate 2:8:0.16 and (f) nanofiber of chitosan/PVA-sodium silicate 2:8:0.32

Figure 3. TGA curve of nanofiber of chitosan/PVA 6:4 (a), chitosan/PVA-sodium silicate 6:4:0.32 (b), chitosan/PVA 5:5 (c), chitosan/PVA-sodium silicate 5:5:0.32 (d), chitosan/PVA 2:8 (e), chitosan/PVA-sodium silicate 2:8:0.32 (f).

It is in accordance with the research of [17], the higher quaternary ammonium chitosan (HTCC) content increases the HTCC/PVA fiber thermal stability. The increasing stability of fiber thermal can be explained by the presence of HTCC that has higher thermal conductivity. HTCC/PVA fiber thermal stability increases as compared to PVA fiber without HTCC. According to [6], the melting point of PVA fiber is (228 ± 5) °C while PVA/CS with weight ratio composition of (90/10)% has melting point of (224 ± 3) °C higher than PVA/CS (50/50)% with melting point (218±3) °C. These results indicate that the presence of CS in CS/PVA fibers reduces PVA crystallinity percentage in the fiber and destroys PVA crystallinity.

Silica fiber with non-polar organic groups (-OR) on the matrix depends on its hydrophobicity that has low thermal stability. Hydrophobicity can be easily destroyed by decomposing non-polar organic groups (-OR) on the matrix. Polydimethylsiloxane (PDMS) to increase thermal stability in silica fiber/PDMS. Organic groups in PDMS begin to decompose at 330 °C. Increased siloxane groups (Si-O-Si) from PDMS are thought to cause thermal stability to increase in silica/PDMS fiber [19]. In line with the study of [19], the addition of sodium silicate to CS/PVA polymer solutions do not increase the fibers thermal stability produced and the possibility of the Si-O-Si group is not formed. This result is supported by FTIR data which shows Si-O-Si at 1080 cm⁻¹ wave number which should be present on CS/PVA-sodium silicate fiber that is not clearly visible.

The hydrophilicity of the produced fiber was tested by immersing the fiber in a buffer solution with a pH of 4.0 and 7.0 for 24 hours. Swelling Index (SI) values are calculated using equation 1. Test results for membrane hydrophilicity are presented in Figure 4.
Figure 4. The Swelling Index (%) on various compositions of chitosan/PVA-sodium silicate fiber

Water absorption at pH = 4 that has been done on electrospun of chitosan/PVA-sodium silicate fibers, obtained the highest degree of distortion in electrospun fiber sample A that is equal to 18.20%, while the lowest degree of distortion obtained by membrane F, G, and H that is equal to 9.09%. Water absorption at pH = 7 that has been done on electrospun chitosan/PVA-sodium silicate fiber, obtained the highest degree of distortion on sample A that is equal to 15.38%, while the lowest degree of distortion obtained by sample J that is 4.54%. Generally, it can be concluded that the increase of silica concentration decreases hydrophilicity and vice versa, the increase in PVA concentration increases the hydrophilicity as the pH value increases. PVA is a polymer that has quite a lot of –OH groups and is hydrophilic so that the absorption properties on water are increasing [13]. It is in accordance with [20], the increase of PVA content in CS/PVA fibers increases hydrophilicity which is characterized by the decreasing contact angle of CS/PVA fibers. According to [6], the addition of SiO$_2$ to 6% mass can reduce water absorption or hydrophilic properties that decrease to hydrophobic properties. Nanofiber CS/(PEO)/SiO$_2$ 30/70 wt% shows low swelling, increased silica content causes roughness level in the resulting fiber surface morphology [4].

4. Conclusion
CS/PVA-sodium silicate fiber is successfully synthesized using electrospinning method. The addition of sodium silicate solution to CS/PVA polymer solution increases the percentage of fiber diameter to be <100 nm and increases fiber uniformity, especially in chitosan/PVA polymer mixture with volume ratio of 2:8. Increasing PVA content in CS/PVA polymer solutions increases the percentage of fiber diameter to be <100 nm and increases uniformity of fiber, and vice versa increasing CS content decreases the percentage of fiber diameter to be <100 nm and decreases fiber uniformity (bead shaped). The addition of sodium silicate solution to chitosan/PVA polymer solution reduces the CS/PVA-sodium silicate fibers thermal stability but increases the CS/PVA-sodium silicate fibers hydrophilicity.

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