Electrospun of Poly (vinyl alcohol)/ Potassium hydroxide (PVA/KOH) nanofiber composites using the electrospinning method

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Abstract. The Poly (vinyl alcohol)/Potassium hydroxide (PVA/KOH) nanofiber Composites for application as a supercapacitor electrolyte. Electrospinning method has been successfully used to synthesize composite of the PVA/KOH nanofiber. The PVA and KOH have been made with concentration are 5% w/w (PK1), 10% w/w (PK2) and 15% w/w (PK3), with a mass ratio of PVA/KOH is 10:1. The Physicochemical properties of PVA/KOH nanofibers with three various in the experiment were studied, including morphology, size, and chemical interaction. The microscope result shows that nanofiber of PK1, PK2 and PK3 have bead fiber and free-bead fiber, Where the PK1 is bead fiber and the PK2 and PK3 are free-bead fiber. The average diameter of PK1, PK2 and PK3 were 635, 826, 1021 nm, respectively. The FTIR results show that there is interaction between Poly (vinyl alcohol) and Potassium hydroxide (KOH) in the form of a spectrum and widening of transmittance are 3320 cm-1 and 3301cm-1 which identifies hydrogen bonds.

1. Introduction

Electrospinning was a spinning method used to produce microfiber to nanofiber [1-4]. The main components of electrospinning are the syringe, syringe pump, high voltage power supply, and collector [1,2,5]. The supporting components are charge-couple device (CCD) camera, monitor, humidity sensor [1,5]. The use of this apparatus starts with a voltage adjusted by high voltage power supply on a syringe that has a polymer solution. Polymer solutions will be attracted by the formation of a Taylor cone at the tip of the syringe and produce fiber on the collector [5,6]. The fiber formation was controlled through parameters such as viscosity, polymer, conductivity, voltage, a distance of the syringe tip to the collector, and flow rate [7]. Application of fiber produced through electrospinning methods for example tissue engineering [8], water filtration [9], air filtration [10], wound dressing [11,12], drug delivery [13,14], batteries [3] and supercapacitor [2,15].

The material used to produce fiber can come from various polymer syntheses through a combination of other materials, for example the synthesis of Poly (vinyl alcohol) (PVA) and Potassium hydroxide (KOH). PVA was chosen because it has high dielectric, semi-crystalline, non-toxic and low prices. But at high temperatures, there is instability in ionic conductivity [16]. This condition can be overcome through PVA synthesis with KOH, where KOH has a low melting point and high ionic conductivity

[17]. Comparison of ionic conductivity Lithium hydroxide (LiOH) 38,69 S.cm^2/mol and Sodium hydroxide (NaOH) 50,11 S.cm^2/mol lower than Potassium hydroxide (KOH) 75,51 S.cm^2/mol [18]. The synthesis of this second material is called PVA/KOH nanofiber composite which can be applied as an electrolytic capacitor. Electrolytes are ionized materials that become electrical conductors. KOH is a strong electrolyte because it is capable of perfectly ionizing into ion K and ion OH [19]. PVA-based electrolyte studies have been reported for example PVA/SC[20], PVA/$LiCF_3SO_3$ [21], PVA/Chitosan [22], However, PVA/KOH nanofiber composites have never been reported.

In this study we have synthesized PVA/KOH composite nanofiber using the electrospinning method. The morphology and diameter of the nanofiber were observed using a digital microscope and the chemical interactions between PVA and KOH were investigated using Fourier Transform Infrared Ray (FTIR).

2. Experimental methods

Synthesis of PVA/KOH nanofiber using PVA with MW 89.000 g/mol, KOH with MW 56 g/mol and distilled water (H_2O). Both materials are dissolved into distilled water respectively, where the PVA solution are set at concentrations at 5%, 10% and 15% (w/w). through stirring for 60 minutes at 60°C. While the concentration of KOH solution is set at 2.5% (w/w) without stirring. Then, both solutions are synthesized with a mass ratio of 10:1 and stirred again for 90 minutes at 80°C. After compositing each solution is labeled PK 1, PK 2, and PK 3 as intended in table 1.

Table 1. Formula sintesis PVA/KOH.

Label	Concentration PVA % (w/w)	Concentration KOH % (w/w)	Mass Ratio
PK 1	5	2,5	10:1
PK 2	10	2,5	10:1
PK 3	15	2,5	10:1

The solution is inserted into the syringe, then the electrospun uses electrospinning apparatus (Nachriebe 601) illustrated in the schematic Figure 1. Throughout electrospun, the 0.8 mm diameter syringe is placed in the humidity chamber (RH 60%). The solution flows due to being driven by the pump with speed 40 μl/h. Voltage 19 kV DC given so that the solution is pulled towards collector, it is required to establish a Taylor cone monitored using a charge-coupled device camera (CCD-Camera). The nanofiber is collected in a drum-shaped collector that has a speed of 200 rpm and the distance of the syringe tip to the collector is 10 cm.

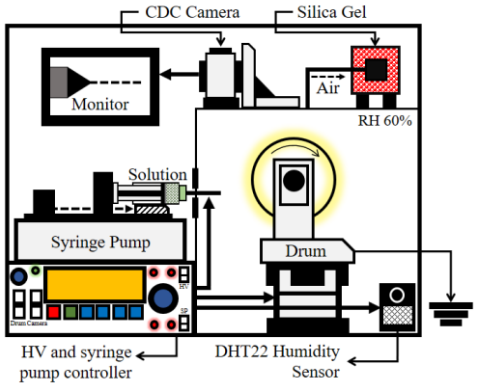

Figure 1. Schematic illustration of electrospinning apparatus.

The morphology of PK 1 nanofiber, PK 2 and PK 3 was observed using a digital microscope. The diameters of PK 1 nanofiber, PK 2 and PK 3 were measured using Image J 1.52a and the size distribution

was analyzed using OriginPro 2018 ver. 9.5. The chemical interactions of PK1, PK2 and PK3 nanofiber were investigated using the Fourier Transform Infrared Ray (FTIR) spectrum range 500 – 4000 cm^{-1}.

3. Results and discussion

3.1. Poly (Vinyl alcohol)/ Potassium hydroxide image

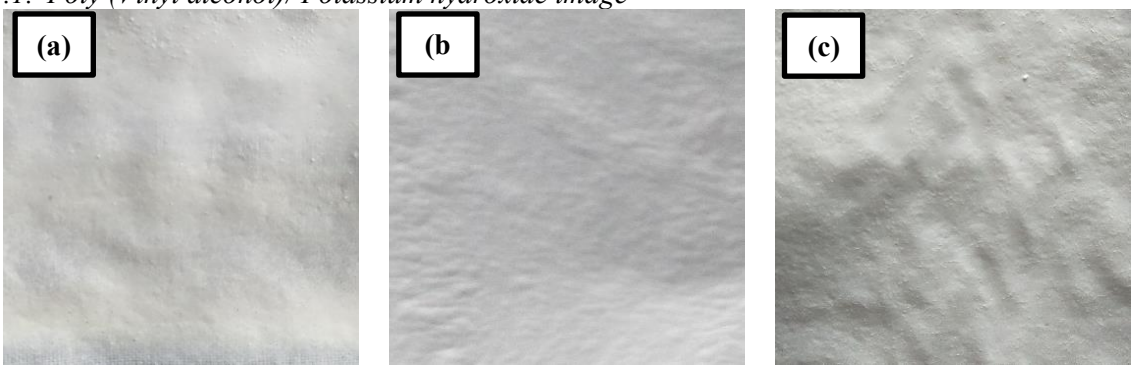

Figure 2. Nanofiber PVA/KOH (a) PK1, (b) PK 2, (c) PK 3.

The microscopic electrospun results using the electrospinning method are shown in figure 2. PK 1, PK 2 and PK 3 nanofiber has elastic, flexible, smooth white surface and is homogeneous. The formation of nanofiber is influenced by the balance between PVA/KOH solution and electrospinning process parameters. The mass ratio of PVA/KOH solution which is 10:1 is the maximum composition to produce the optimum nanofiber. Electrospun starts with synthesizing PVA and KOH. After composite, the solution is put into the syringe placed on the syringe pump. Then the solution is driven with a constant regulated speed. The DC voltage source is connected to the end of the syringe, acting as a positive electrode. Meanwhile, the negative electrode is the drum collector. These electrodes can be exchanged for poles. When the two electrodes are subjected to a very high electrical voltage, the solution which is initially totally neutral will be polarized due to the influence of the second potential difference of the electrode. If the syringe is connected to the positive pole of the DC voltage source, the surface of the solution will accumulate positive ions, while the negative ions gather in the middle such that the total electric field due to the polarization of the ions reaches zero [23]. Conversely, if the needle is connected to the negative pole of the DC voltage source, the negative ions accumulate on the surface of the solution, while the positive ions polarize in the middle of the solution. The charge in this polymer solution is spread throughout all parts of the solution, including on the surface of the solution. The accumulation of charges in solution causes the appearance of the Coulomb repulsive force between charges with the equation:

$$\vec{F}_c = k\frac{q_1 q_2}{r_{21}^2} \tag{1}$$

with Coulomb force and electric force due to the field between the two electrodes, namely:

$$F_{electric} = q\vec{E} \tag{2}$$

The influence of Coulomb force causes the polymer solution to be attracted to form a cone called Taylor Cone as shown in figure 3. When the resultant of these two forces exceeds the surface tension force of the polymer solution, which works in contrast to the Coulomb force and the electric force the charged polymer solution is accelerated by an electric field towards the collector, so that the polymer solution is attracted to and emits a very small size. As long as the polymer solution is attracted, the polymer undergoes elongation and the solvent evaporates due to the influence of the high voltage applied, so that the polymer formed at the surface of the collector is in the form of fiber in solid form [6,24].

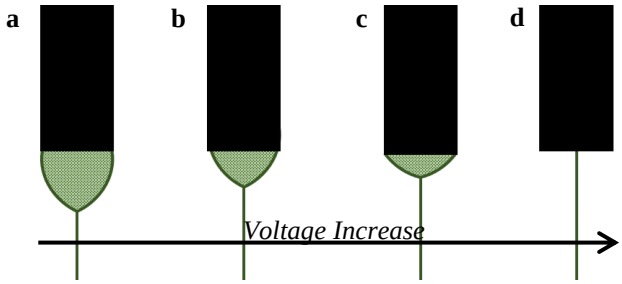

Figure 3. Illustration of a cone jet model if voltage is increased.

3.2. Morphology and diameter PVA/KOH nanofiber

The morphology and diameter distribution of PVA/KOH nanofiber is shown in Figure 4. PVA/KOH composites at low concentrations (5% (w/w) produce bead fiber, while at high concentrations (10% and 15% (w/w)) produce free-bead fiber. The morphology formed is influenced by viscosity which is a measure of the thickness of a fluid in inhibiting the fluid force, expressed in the concentration of the solution [25]. Viscosity also represents the extent to which the polymer chain attaches in solution. At low conditions the interaction between solvent molecules is more dominant than the interaction between polymer molecules and the interaction between polymer molecules and solvent molecules. Thus, the chain of bonds of polymer molecules is produced too little and evaporation of the air is faster as a result of bead fiber. In addition, solutions with low viscosity tend to form smaller size nanofiber while high viscosity solutions produce nanofiber of a larger size or free bead [26]. In this study, nanofiber diameter sizes increased from low concentrations (5% (w/w)) to high concentrations (15% (w/w)) such as PK 1 (635 nm), PK 2 (826 nm), and PK 3 (1021 nm).

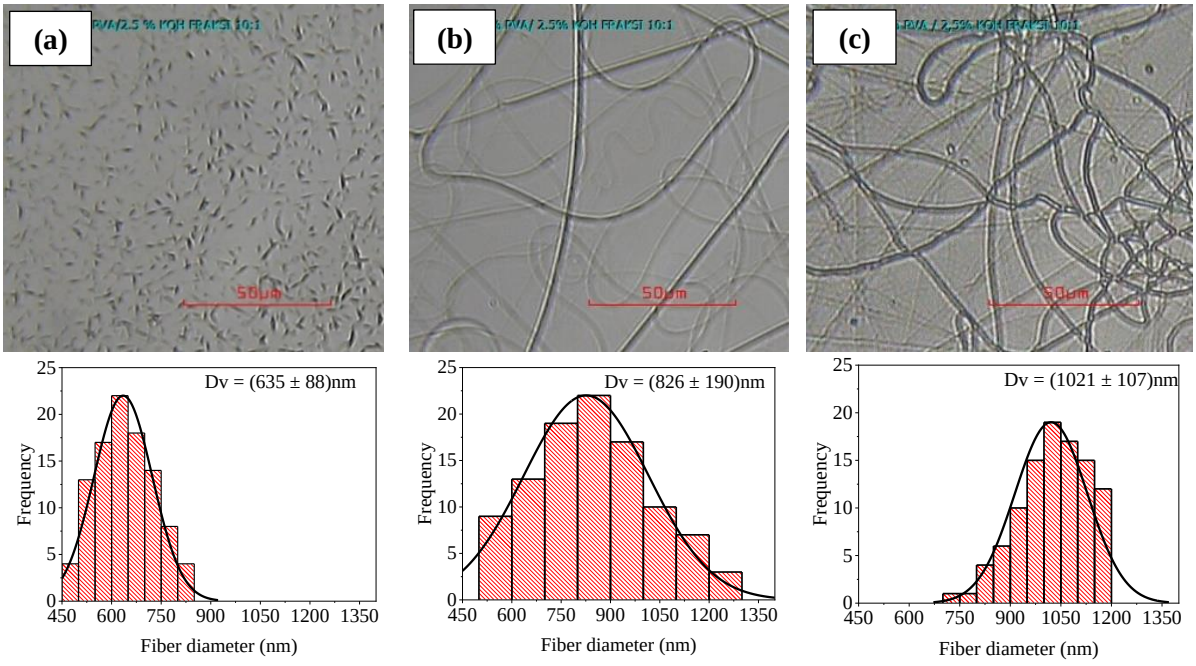

Figure 4. Morphology and diameter distribution of nanofiber (a) PK 1, (b) PK 2, and (c) PK 3.

3.3. FTIR analysis

FTIR is used to detect specific groups of polymers. The wave number used is in the range 500-4000 (cm^{-1}). Figure 5 showing the FTIR PVA spectrum, the peaks of PVA molecular transmittance are 3297 cm^{-1} a O-H stretching on the hydroxyl group, and peak 2942 and 2914 cm^{-1} identify asymmetrical and

symmetrical CH2 stretching on alkyl groups [27–29]. Peak 1714 cm^{-1} identify absorption H_2O and peak 1427 cm^{-1} and 1244 cm^{-1} shown CH_2 beading while strengthening the bond between OH and CH [27–29]. While 1141 cm^{-1} and 1083 cm^{-1} each identifies a C−O stretching on ester groups, C=O stretching on aldehyde groups [27,29]. 916 cm^{-1} and 840 cm^{-1} each identifies CH_2 rocking and C–C rocking alkyl groups. Figure 6 show the KOH FTIR spectrum, the molecular transmittance peaks of KOH are 3500 cm^{-1} and 1405 cm^{-1} a OH strengthening in the hydroxyl group. Peak 1749 cm^{-1} and 1660 cm^{-1} identify absorption H_2O. While 885 cm^{-1} and 654 cm^{-1} identify the bond between K–O [19,30,31].

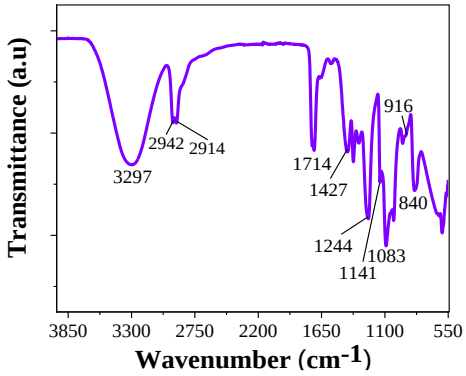

Figure 5. FTIR spectrum of Poly(vinyl alcohol) (PVA).

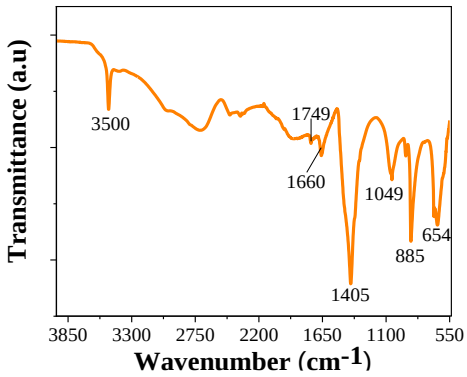

Figure 6. FTIR spectrum of Potassium hydroxide (KOH).

The results of PVA/KOH FTIR analysis of PK 1, PK 2, PK 3 nanofiber as in figure 7 show the change in intensity of PVA transmittance when combined with KOH. Addition of PVA in PVA/KOH concentrations also caused changes in peaks of PK 1, PK 2 and PK 3 nanofiber. First, in the range of 3800-3000 (cm^{-1}) there was an increase in the intensity of transmittance, where PK 3 nanofiber had a peak greater than PK 1 and PK 2. In this range, the three nanofiber have a tendency to peak similarity to the PVA. The increase in concentration causes an O–H shift in the hydroxyl group towards a larger number PK 1 (3301 cm^{-1}), PK 2 (3307 cm^{-1}) and PK 3 (3320 cm^{-1}).

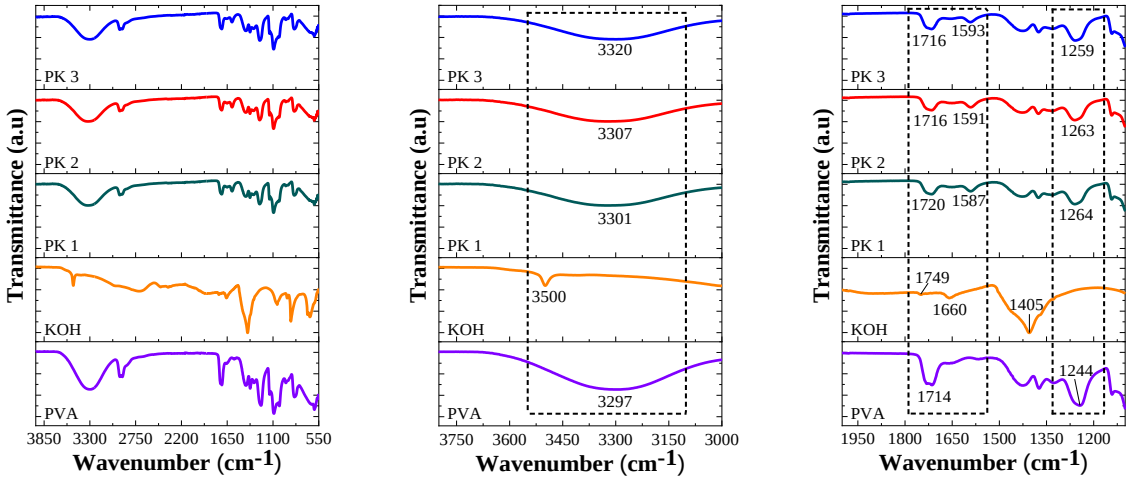

Figure 7. FTIR spectra of PVA/KOH PK 1, PK 2 and PK 3 nanofiber.

Second, the increase in PVA in PVA/KOH causes absorption by water to increase in the range 2000-1100 (cm^{-1}). When observed, PK 1 (1720 cm^{-1}), PK 2 (1716 cm^{-1}), PK 3 (1716 cm^{-1}) nanofiber weakened PVA transmittance (1714 cm^{-1}) which is very significant, this indicates that PVA is hydrophilic. Then, peak appearance PK 1 (1587 cm^{-1}), PK 2 (1591 cm^{-1}), PK 3(1593 cm^{-1}) indicates KOH interaction (1660 cm^{-1}) through absorption H_2O, where KOH is a strong base that is also hydrophilic. Third, an increase

in PVA/KOH nanofiber makes a peak shift PK 1(1264 cm^{-1}), PK 2 (1263 cm^{-1}), PK 3 (1259 cm^{-1}) with increasingly sharp transmittance, this condition shows CH2 beading while strengthening the bond between OH and CH. Changes in peak FTIR in PK 1, PK 2 and PK 3 are seen as the result of PVA/KOH interactions.

4. Conclusion

PVA/KOH nanofiber has been successfully synthesized using the electrospinning method. PVA/KOH nanofiber is divided into PK 1, PK 2 and PK 3 characterized in the morphology, diameter and interaction of the PVA/KOH molecular chain. The three nanofiber have a morphology of elastic, flexible, smooth, white and homogeneous texture. The results of the microscope show that PK 1 is a fiber bead and PK 2 and PK 3 are free-bead fiber. The average diameter size of PK1, PK2 and PK3 is 635, 826, 1021 nm. FTIR results showed peaks between the hydroxyl OH group bonds, H_2O bonds by H_2O absorption, and CH_2 beading as well as strengthening the bond between OH and CH. Changes in peak FTIR in PK 1, PK 2 and PK 3 are seen as the result of PVA/KOH interactions.

Acknowledgments

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