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Synthesis and Characterization of PANI/PVA Nanofibers with Variation of Nozzle to Collector Distance Using Electrospinning Method

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ABSTRACT

FTIR confirmed fumaric acid doped polyaniline as a polyaniline emeraldine salt phase. This study aims to determine the value of the electrical conductivity of PANI/PVA with variation in the distance of the needle to the collector, namely 11 cm, 13 cm, 15 cm, and 17 cm. The electrospinning method was carried out on a PANI/PVA solution to form polyaniline nanofibers. The electrospinning solution used a percent ratio of 1:1 PANI/PVA (10%). The morphological and fiber properties were characterized using FTIR, optical microscope, and SEM-EDX. The number of fibers decreases and becomes more delicate as the distance increases due to the evaporation of PVA. The diameter of PANI/PVA fiber and pure PVA fiber are 236 nm and 256 nm. The PVA fiber diameter is slightly larger than the PANI/PVA fiber. Electrical conductivity was carried out using the four-point probe method. The electrical conductivity of the PANI/PVA sample is 1.39 × 10^{-6} S/cm at a distance of 15 cm with the best fiber shape.

Introduction

Polyaniline (PANI) has become one of the most studied conducting polymers due to its simple and low-cost synthesis, unique redox properties, high conductivity, and excellent environmental stability [1]. Polyaniline (PANI) has been widely developed in electronic devices such as sensors, capacitors, batteries, organic light-emitting diodes (OLED), and organic photovoltaic cells (OVC). In applying polyaniline as a sensor, polyaniline can be converted into nanofiber form because it is very effective and has a much larger surface area [2]. Polyaniline (PANI) can be synthesized in several forms of oxidation phase, including fully reduced Leucomeraldine Base (LB), partially oxidized Emeraldine Base (EB), and fully oxidized Pernigraniline Base (PB). An emerald phase base an can be conductive by doping with an acid. Protonations are added to the –N= region (EB form) while the number of electrons in the chain remains [3]. Intrinsically conductive polymer material Polyaniline (PANI) has unique electrical properties because it can be an insulator or conductor where the conductivity values range from 10^{-9} to 10^{-2} S/cm [4].

The methods used for the synthesis of PANI are chemical and electrochemical. The chemical polymerization method can produce PANI in powder form. There are two kinds of chemical method: the oxidation method and the interface method. Using the chemical oxidation method can produce polyaniline powder in sufficient quantities, so it is advantageous to apply it [5]. Doping strong acid (HCl, H_2SO_4) in the polymerization process of polyaniline can increase the conductivity higher than doping with a weak acid (fumaric acid). However, PANI with fumaric acid dopant has better solubility in polar organic solvents. With fumaric acid dopants on the PANI backbone, the interaction of the PANI backbone becomes weak; the PANI backbone can gain space, and the polymer becomes easily soluble in polar solvents and allows penetration of solvent molecules in the chain [6]. Polyaniline with low concentration is quite sensitive when used as a sensor because the nanostructure of polyaniline has a fairly large solubility in suitable solvents [2]. So that polyaniline can be fabricated as nanofiber.

Nanofiber is a material produced by nanotechnology. One of the methods used to produce nanofibers is the electrospinning method [7]. *Electrospinning* is a method that can produce ultrafine fibers with diameters in the nanometer-to- micrometer range [8]. Nanostructures by the electrospinning method can be applied in various fields. One of them is as a sensor application. Parameters of nanofiber fabrication using the electrospinning method include voltage magnitude, nozzle to collector distance, and solution concentration [7]. In the nozzle to collector distance parameter, the structure and morphology of the fiber are caused by the instability and the capture time of the fiber to the collector. With a shorter time, there is no opportunity for the solvent to evaporate so it will help the formation of beads on the fiber [9]. The advantage of nanofiber as a sensor is that it has a large surface area [10] to increase sensitivity and responsiveness [2]. Informing a conducting fiber, combining a conducting polymer and a non-conducting polymer is required.

However, the disadvantages obtained are low electrical properties compared to pure conducting nanofibers designed using electropolymerization and electrodeposition [11]. The conducting polymer used is PANI, and the non-conducting polymer is PVA. As a conducting polymer, PANI is not easily made into pure polyaniline nanofibers because of its insoluble nature and high molecular weight. Therefore, other polymers are needed to mix polyaniline and help the formation of nanofibers. One of them is PVA [12]. PVA has properties that are soluble in water, easy to process, non-toxic, biocompatible, biodegradable, and can be a carrier polymer in the formation of nanofibers. Several studies have shown that the results of PANI/PVA nanofibers show fine fibers [13], and the fibers contain large beads [12], which show resistance to the aluminum foil substrate [14], and homogeneous fiber shape [13]. In this study, PANI/PVA nanofibers were produced, and their electrical conductivity was measured, which had not been done in previous studies [15]. In several studies that have been carried out, the effect of distance on the electrical conductivity of PANI/PVA nanofibers has not been explained [16][17]. In this study, the synthesis of PANI/PVA nanofibers using the electrospinning method has been carried out with variations in the nozzle to collector distance.

The aim is to determine the effect of the nozzle to collector distance on the morphology and electrical conductivity of PANI/PVA nanofibers.

Experimental Method

This research is experimental research conducted in the material laboratory of the Physics Department, Universitas Negeri Surabaya. The variables in this study consisted of control variables, namely PVA concentration (10%) and 15kV voltage. In contrast, the manipulation variable was the distance of the needle to the collector (11 cm, 13 cm, 15 cm, and 17 cm).

Fumaric acid doped PANI synthesis

Polyaniline was synthesized by the chemical oxidation method, which dissolved 2.9 g of fumaric acid into 25 mL of distilled water and stirred using a magnetic stirrer for 30 minutes. Aniline is then added to the fumaric acid solution. Then 2.85 g of ammonium peroxydisulfate $(NH_4)_2S_2O_8$ was added, dissolved in 25 mL of distilled water and then allowed to stand for 4 minutes while stirring. Then left for 24 hours for polymerization to occur. The PANI precipitate formed was then washed with 0.2 M HCl, washed again using 10 mL acetone, and the last washed with distilled water. The PANI precipitate was dried at 60^0C for 24 hours to form PANI and then sieved.

Preparation of PANI/PVA Nanofibers

PANI/PVA nanofibers were manufactured by making a PVA solution with a concentration of 10%. One gram of PANI powder was mixed into the PVA solution by ultrasonication for 50 minutes. The solution was stirred for 30 minutes, and a PANI/PVA solution was formed. Electrospinning PANI/PVA solution with a voltage of 15kV and the distance from the tip of the needle to the collector of 11 cm, 13 cm, 15 cm, and 17 cm for 1 hour for each distance.

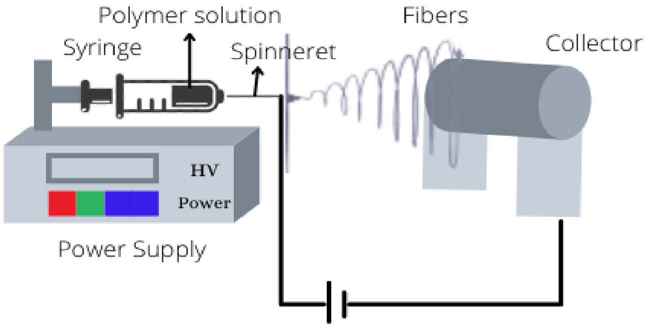


Figure 1. Schematic of the electrospinning tool

Characterization

The synthesized polyaniline samples and PANI/PVA nanofibers were characterized using Fourier Transform Infrared (FTIR) in the Laboratory of the Department of Materials and Metallurgy, Institut Teknologi Sepuluh Nopember to determine the type of bond and morphological tests using an Optical Microscope in the Laboratory of IDB, Universitas Negeri Surabaya to determine the shape of the electrospinning fiber, and Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) in the Laboratory of Mechanical Engineering, Institut Teknologi Sepuluh Nopember to show the material being contained in the PANI/PVA nanofiber samples and to determine the fiber diameter distribution.

The PANI/PVA nanofiber will also be tested for conductivity using the Four-Point Probe (FPP) method. This thick sheet requires that the sample thickness (*t*) be less than the distance between the probes (*s*). Because at the tip of the outer probe is the current supersede, then [18].

$$R = V/2I \qquad (1)$$

$$\rho = \pi t/(Ln\ 2)(V/I) \qquad (2)$$

So the conductivity is:

$$\sigma = 1/\rho \qquad (3)$$

Result and Discussion

Fumaric acid doped PANI powder from the polymerization process using the chemical oxidation method was identified by FTIR to determine the type of bond formed, as shown in Figure 2.

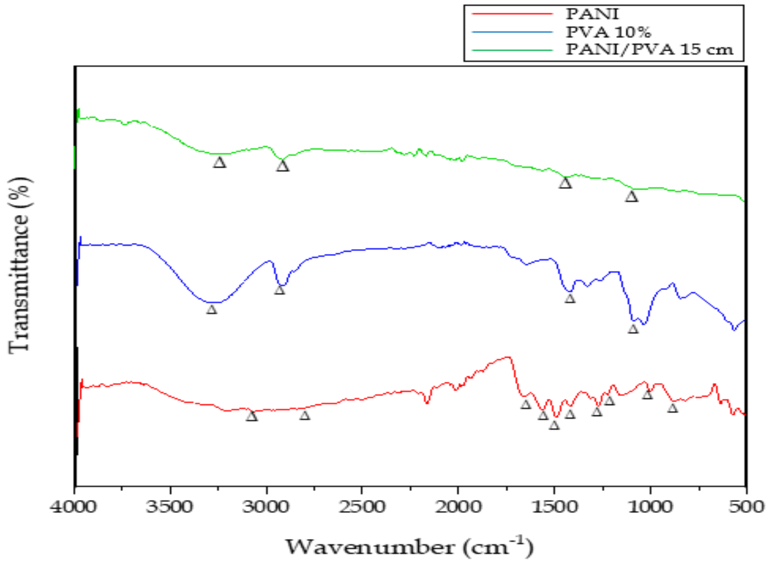


Figure 2. Results of PANI, PVA, and PANI/PVA FTIR spectra

Table 1. Functional Groups for PANI [6]

Wavenumbers (cm^{-1})			Functional Groups
Datasheet	***Ref (PANI)**	**Sample PANI**	
	3082.16 – 2523.21	3081.68	N-H *stretching vibration*
	1682.44	1682.37	C = O *stretching vibration*
1650-1560	1567.87	1634.68 – 1568	C = C *stretch* (Q)
1500-1400	1494.92	1495.06	C = N *stretch* (Q), C-C *stretch* (B)
1335-1250	1270.81	1270.87	C-H *bending* (Q)
1250-1020	1228.82	1228.27	C-N *stretch*, C-C *stretch*, C-H *bending* (B)
1250-1020	1130.70	1157.22	Efek dopan
850-550	876.56	876.08	C-H *bending*

Table 2. Functional Groups for PVA and PANI/PVA [6][13][12]

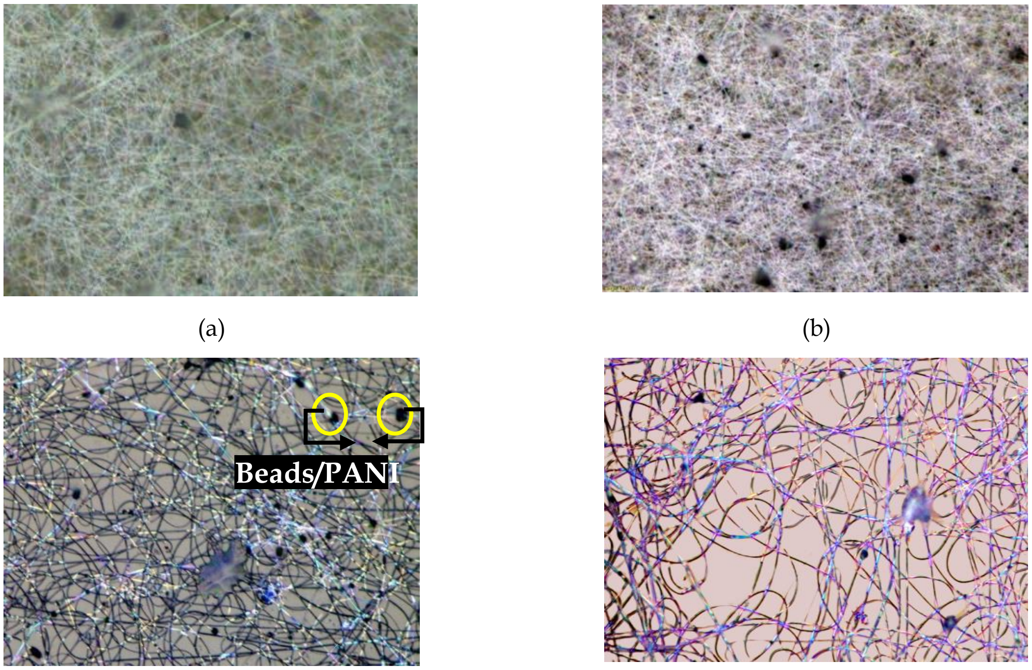
Wavenumber (cm^{-1})			*Functional Groups PVA	*Functional Groups PANI/PVA
Datasheet	**Sample PVA**	**Sample PANI/PVA**		
3550-3200	3285.84	3278.10	O-H *stretching*	O-H *stretching*
2840-3000	2915.84	2910.82	CH_2 *stretching*	CH_2 *stretching vibration*
	1415.99	1444.85	C=C *stretching*	C=N *stretch* (Q)
1150-1085	1088.10	1090.24	C-O-C	Efek dopan

Figure 2 shows the results of testing the infrared spectrum for samples of PANI in Table 1, PVA nanofibers, and PANI/PVA nanofibers in Table 2. The difference in the nozzle to collector distance of the PANI/PVA nanofiber did not affect the shift in the FTIR Spectrum so only one sample was tested for FTIR. FTIR Spectrum Shift can occur if the PANI composition is added to the nanofiber composite [17]. From the results of the FTIR test, it is known that PANI is in the ES phase with absorption peaks following the polyaniline functional group shown in Table 1. The functional groups in a molecule are determined when the molecule absorbs energy in the infrared causing the bonds in the molecule to vibrate [6]. The types of bonds formed include N-H stretching vibration, C = O stretching vibration, C = C stretch (Q) at, C = N stretch (Q) and C-C stretch (B), C-H bending (Q), C-N stretch and C-C stretch, C-H bending (B), and dopant effect. The results of this study correspond to previous studies [6].

Synthesis of PANI/PVA nanofibers was carried out by the electrospinning method. The FTIR test results for PANI/PVA nanofibers produced several types of bonds in the wavenumber range of 400-4000 cm^{-1}. Figure 2 shows the pure PVA functional groups, namely O-H stretching and CH_2 stretching vibration. After adding polyaniline to PVA, there was a shift in the O-H stretching and CH_2 stretching vibration spectrum peak. There is a shift in wave peaks between pure PVA and PANI/PVA samples, including stretching vibration CH_2, which is 5.02 cm^{-1} and O-H stretching is 7.74 cm^{-1}. This shift in wave peaks is due to the formation of the PANI/PVA composite.

Table 3. PANI/PVA Nanofibers Diameter.

Voltage (kV)	Distance Nozzle to Collector (cm)	Diameter of PANI/PVA Nanofibers (μm)
15	11	0.53
15	13	0.50
15	15	0.33
15	17	0.42



(a) (b)

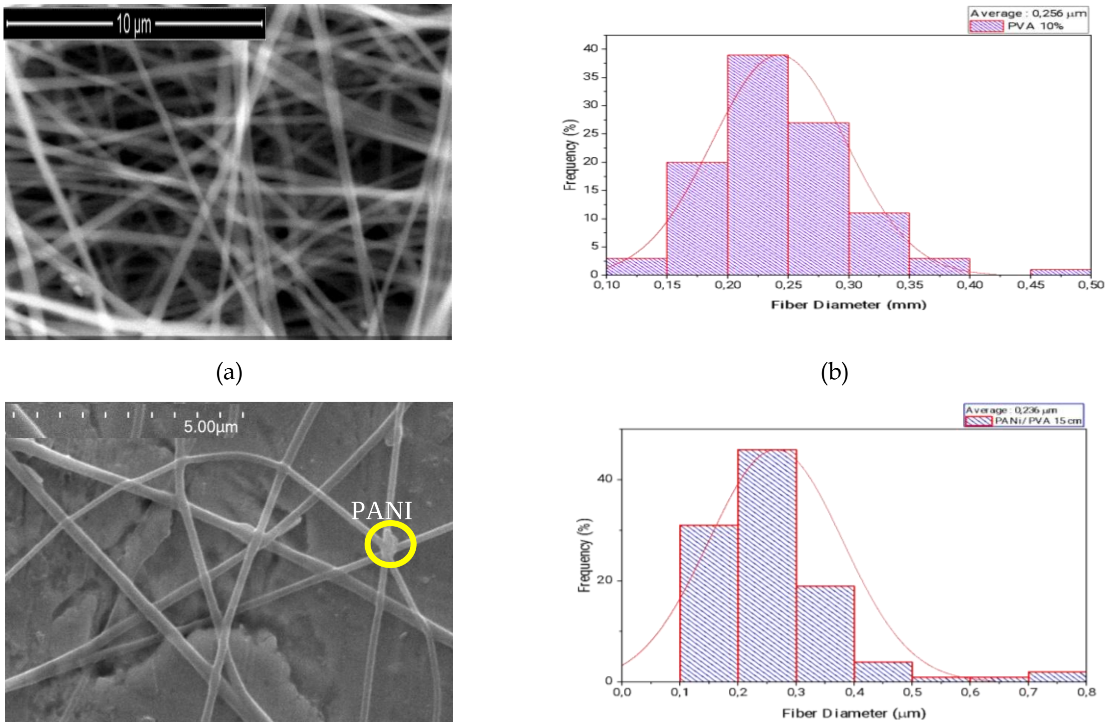
(c) (d)

Figure 3. Morphology of PANI/PVA nanofibers: (a) J11, (b) J13, (c) J15, (d) J17 with Optical Microscope (Magnification 50×)

Morphological results depend on the parameters of the synthesis process. In this study, distance parameters were used in the formation of nanofibers. PVA is used as a binder to form PANI/PVA fibers. Figure 3 shows the results of optical microscope observations with a magnification of 50 times. These results indicate that the increasing distance of the nozzle to the collector will cause the fiber density to decrease. The fiber density decreases due to the increase in polymer discharge instability, where the fibers coming out of the nozzle tip are not completely captured by the collector or bending occurs. This bending causes the formation of beads in the fiber morphology [7].

The J11 and J13 nanofiber morphology observations showed that the fiber was denser than the other sample. At a distance of 10 cm from the needle to the collector and a voltage of 15 kV, it produces dense fibers [17] as in samples J11 and J13. While on J15 and J17, the fibers are more-stretchy, and there were many beads. The beads are PANI powder which is not completely dispersed.

Observing and analysis were carried out with an optical microscope to determine the effect of distance to the collector on fiber diameter and sample morphology. Table 3 shows the diameters of PANI/PVA fibers J11, J13, J15, and J17 with a constant voltage of 15kV and a flow rate of 1mL/hour. The increasing distance of the needle to the collector with the same voltage treatment of 15kV can cause the fiber diameter to decrease with increasing polymer release instability [7], with differences in distances of 11 cm, 13 cm, 15 cm, and 17 cm from the distance of the needle to the collector. Diameters are 0.53 μm, 0.50 μm, 0.33 μm, and 0.47 μm, respectively. The relationship between voltage and flow rate is not linear, so a minimum diameter of 0.33 μm is obtained for a distance of 15 cm [16].



(a) (b)

(c) (d)

Figure 4. (a) PVA SEM image, (b) 10% PVA fiber diameter normal curve distribution, (c) PANI/PVA SEM image, (d) PANI/PVA J15 fiber diameter normal curve distribution

PVA fiber morphology in Figure 4(a) with a dense fiber morphology at 15k times magnification. Using ImageJ software shows that the average diameter of PVA fiber is 256 nm (Figure 4b). The PANI/PVA composite fiber with a magnification of 10k times can be observed in Figure 4(c). The SEM PANI/PVA was carried out on sample J15 because this sample produced a minimum diameter based on the influence of the distance parameter where the test was carried out with an optical microscope, which shows the formation of a fiber with a relatively homogeneous size, not broken or cut, and there are several beads. The results of the fiber form follow previous studies [14]. The PANI/PVA J15 sample had an average fiber diameter of 236 nm (Figure 4d). The comparison between the two SEM images shows a clear difference: the PVA fiber diameter is more significant than that of the PANI/PVA fiber. This result was obtained because the solution with electrical conductivity causes a decrease in the diameter of the electrospinning fiber [19].

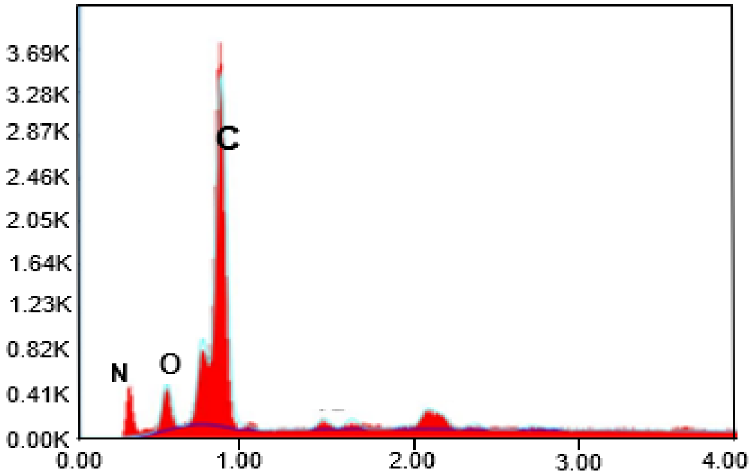


Figure 5. EDAX Nanofiber PANI/PVA J15 (55 μm scale)

The EDAX results from PANI/PVA nanofibers are shown in Figure 5. The elements formed include N, O, and C. The PANI and PVA polymers each have the chemical formulas $C_6H_5NH_2$ and $(C_4H_6O_2)_n$, so the presence of elements C and O from the EDAX results indicates that nanofibers formed were PANI and PVA. The presence of element N proves PANI in PANI/PVA nanofibers.

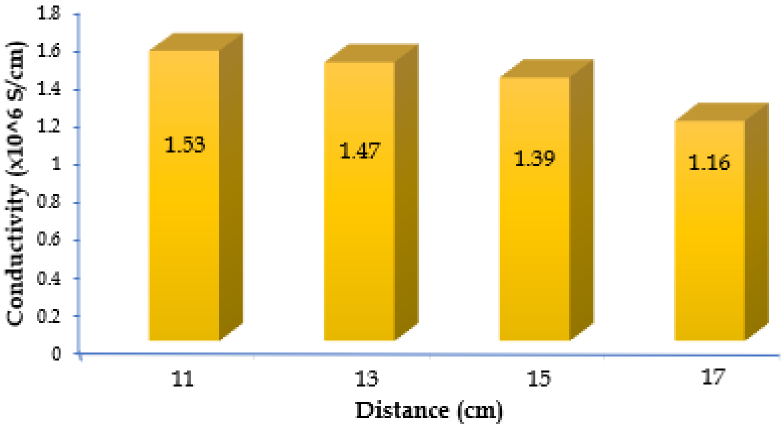


Figure 6. Graph of 10% PANI/PVA conductivity

The results of measuring electrical conductivity using a four-point probe are shown in Figure 6. The conductivity values for each sample (J11, J13, J15, J17) are 1.53×10^{-6} S/cm, 1.47×10^{-6} S/cm, 1.39×10^{-6} S/cm, and 1.16×10^{-6} S/cm. Increasing the nozzle to collector distance can cause a decrease in the PANI/PVA conductivity value. There are fewer PANI beads on PANI/PVA nanofibers at a more significant distance. The highest conductivity is in sample J11, while the smallest conductivity is in J17, where fewer beads are produced on PANI/PVA fiber. The resulting fiber is also more tenuous so that the measured electrical conductivity value will be smaller, causing it to be less conductive.

From the results of this study, the best sample is sample J15 because it has a homogeneous fiber shape, is denser, and there are still some PANI beads; besides that, sample J15 has a relatively large electrical conductivity. An electrical polymer (has a specific conductivity) and the material can absorb water vapor so that there is a change in the electrical properties of the material. The polymer can be used as a humidity sensor [20]. The conductive polymer used in this study is polyaniline. Polyaniline has a conductivity value of about 10^{-9} S/cm to 10^{-2} S/cm [4] and can be applied as a sensor [2]. In this study, the conductivity values were found in the range of $1.53\text{x}10^{-6}$ S/cm to $1.16\text{x}10^{-6}$ S/cm compared to pure polyaniline's conductivity, which was still in that range. The synthesized PANI/PVA nanofibers could be applied as sensors. The sensor application of the PANI/PVA nanofiber sample is as a humidity sensor. In life, humidity sensors can be used for human comfort levels, industrial control, and packaging in food and medicine products [21].

Conclusion

In this study, the synthesis of PANI/PVA nanofibers using the electrospinning method has been successfully carried out with the best diameter based on the SEM test, 236 nm. The measurements using optical microscopy and ImageJ software the difference in diameter was not significant. The best is at a distance of 15 cm. In the measurement of electrical conductivity, it has been proven that significant differences in distance can affect the value of electrical conductivity. The electrical conductivity value from the best PANI/PVA nanofibers measurement was in sample J15 of 1.39×10^{-6} S/cm. This research can be completed properly. Hopefully, the results of this study can provide a reference for future researchers to investigate more deeply, especially those related to electrospun PANI/PVA.

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