

Synthesis and Characterization of PVA/PANI Nanofiber as Active Material for Humidity Sensors

Nugrahani Primary Putri*, Evi Suaebah, Diva Nuri Islami, Lydia Rohmawati, Diah Hari Kusumawati, Fitriana and Zainul Arifin Imam Supardi

Department of Physics, Faculty of Mathematics and Natural Science, Universitas Negeri Surabaya, Surabaya, Indonesia

(*Corresponding author's e-mail: nugrahaniprimary@unesa.ac.id)

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Abstract

PANI is a nanostructure conductive polymer that has been widely researched by making nanofibers using electrospinning, by adding PVA as a non-conductive material. In this research, we have successfully synthesized PVA/PANI nanofiber using the electrospinning method and applied it as a humidity sensor. The oxidation polymerization method was conducted to produce polyaniline (PANI) powder. PVA was used as a non-conductive polymer to carry PANI. PANI is blended with 10 % PVA to produce nanofiber PVA/PANI. The results of the synthesis of PVA/PANI nanofibers using the electrospinning method have been characterized by FTIR and EDX to identify the functional groups and elements of PVA/PANI. The FTIR results confirmed that for the PVA nanofiber samples, the type of polyvinyl alcohol bond has been identified according to the reference. The EDX results show the elements C, O and N. The element nitrogen (N) is the characteristic element of polyaniline ($C_6H_5(NH)_2$)_n. The optical Microscope and Scanning Electron Microscope show that the electrospinning method has succeeded in synthesizing PVA/PANI nanofibers with a fiber size of around 0.313 μ m. The porosity of PVA/PANI is around 55 %, which is related to the ability of PVA/PANI sensitivity to detect humidity. These results are demonstrated by measurements using a Four-Point Probe (FPP), with the humidity value varying from 64 - 80 %. The results show that variations of PANI powder content improve the sensitivity performance of PVA/PANI nanofibers. This method can optimize PVA/PANI nanofiber as a humidity sensor, increase conductivity flexibility, make it easier and enhance the PANI to use as an active sensor.

Keywords: Polyaniline (PANI), PVA, Electrospinning, Humidity sensor

Introduction

Polyaniline (PANI) has become one of the most studied conducting polymers due to its simple and cheap synthesis, unique redox properties, high conductivity and excellent environmental stability [1]. PANI is a conductive polymer composed of aniline monomer ($C_6H_5NH_2$), which is a compound derived from benzene. PANI has several oxidation phases, namely leucoemeraldine (fully reduced), pernigraniline (fully oxidized) and emeraldine (partially oxidized) [2]. Of the 3 phases, only the emeraldine (EB) phase can be converted into a conductive polymer by doping with strong acids such as HCl and H_2SO_4 . With its advantages, namely controllable electrical conductivity, PANI is a promising material that can be applied as a functional sensor material, one of which is a humidity sensor. Many previous studies have employed PANI as a humidity sensor, including PANI/cellulose composites [3], PANI/Cu-ZnS [4], PANI/TNT/rGO [5] and ZnO/PANI [6]. PANI has been widely developed as a conductive polymer in electronic devices such as sensors, capacitors, batteries, organic light-emitting diodes (OLED) and organic photovoltaic cells (OPV) [7].

To apply PANI as an active sensor material, PANI can be formed into nanofiber because it is very effective and has a much larger surface area [8]. Nanofiber is a type of fiber produced using nanotechnology. Various synthesis methods are used, including spin coating, hydrothermal and electrospinning. One method used to produce nanofiber is the electrospinning method and in-situ polymerization [9]. Electrospinning is a method that can produce ultrafine fibers with diameters in the nanometer to micrometer range [10]. Nanostructures using the electrospinning method can be applied in various fields, one of which is as a sensor application. The advantage of nanofiber as a sensor is that it has a large surface area, and it will improve the sensitivity and responsiveness of the sensor [11].

determine the level of porosity, which is correlated with the sensitivity of the sensor. The sensitivity of nanofiber PVA/PANI for humidity sensing was conducted by the Four-Point Probe (FPP).

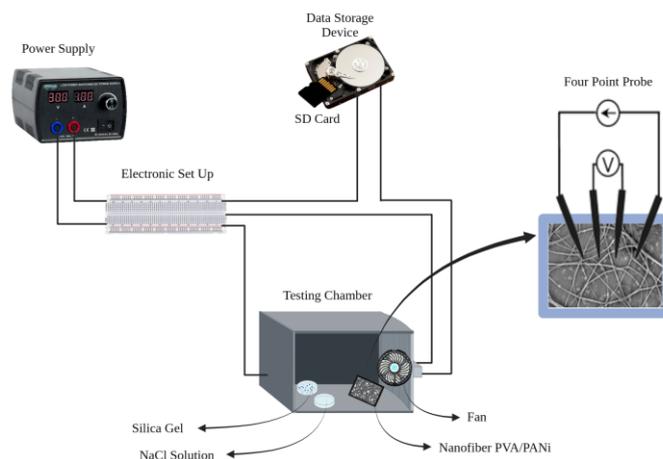


Figure 2 Scheme of four-point probe measurement.

Figure 2 shows the measurement of humidity. The measurement process was carried out by adding salt solution into the chamber to increase the system's humidity. Nanofiber PVA/PANI was detected in the chamber's humidity as initial humidity. Salt in the chamber affected the humidity changes. The addition of silica gel reduces the humidity in the chamber. When humidity changes, nanofiber PVA/PANI will attract, and ions from salt will be trapped on the nanofiber. This change in the number of trapped ions will show a change in resistance from the FPP measurement results. The number of ions trapped in the nanofiber will be proportional to the change in resistance of the measured FPP. The PVA/PANI sensor's measurement of variations in humidity is correlated with the resistivity value. In this case, measurements of humidity were conducted to about 80 %. The limitation of equipment and the maximum humidity in our environment only reaches about 80 %.

Results and discussion

Fourier transform infra-red (FTIR) analysis

Quantitative analysis by FTIR characterization is essential to know the substrate identification of functional groups present in the PVA/PANI nanofiber sample. The FTIR characterization results in a graph depicting the relationship between wavenumber and percent transmittance. The Peaks present at specific wavenumbers will indicate the types of functional groups or bonds in a material. The wavenumber values obtained are compared with reference functional groups from previous research [20]. The FTIR characterization was conducted on PVA and PVA/PANI nanofiber samples. FTIR characterization can show the functional groups of the samples tested.

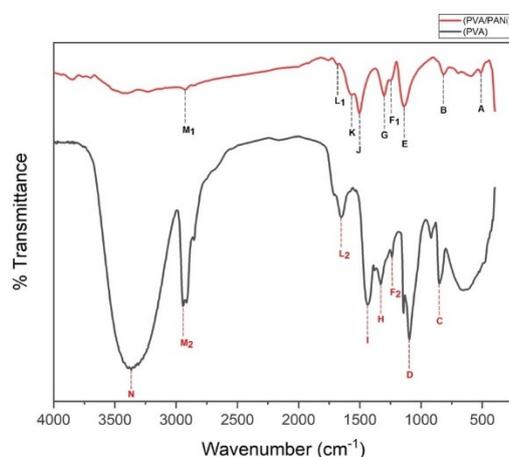


Figure 3 FTIR Spectrum of PVA and PVA/PANI.

Figure 3 shows that the electrospinning technique was successfully performed on PVA nanofiber on PANI. The red spectrum belongs to the PVA nanofiber, while the black spectrum is the FTIR spectrum of the PVA/PANI nanofiber sample, from the results of FTIR characterization at wave numbers between 500 and 4,000 cm^{-1} . The wavelength from 500 until 1,500 cm^{-1} shows the fingerprint region of PVA and PVA/PANI, and the functional group region comes from 1,500 until 4,000 cm^{-1} . Both spectra show the high wave number band at 2,943.47 and 2,924.18 cm^{-1} , corresponding to $-\text{CH}_2-$ stretching. The high number wave becomes weaker, as shown from PVA/PANI, which suggests the PVA was successfully deposited on PANI. For a more explicit identification of bond types, shown in **Table 1**.

The PVA nanofiber samples are types of polyvinyl alcohol bonds. It has been identified according to the reference, including O-H stretching, $-\text{CH}_2-$ stretching, C-H bending and C-C stretching of PVA. For the PVA/PANI nanofiber samples, the presence of PANI has also been identified by the presence of characteristic PANI bonds, namely C=C stretch (Q), C=N stretch (Q), N=Q=N stretching and N-H bonding. The characteristic band of PVA/PANI shifted right compared to pure PVA, ascribed to PANI's effect. It demonstrates that some particular interaction exists between PVA and PANI.

Table 1 Identify the functional groups of PVA and PVA/PANI.

Number of peaks	Wavenumber (cm^{-1})		Bond type	Reference
	Peak PVA (1)	Peak PVA/PANI (2)		
N	3,367.82	-	O-H stretching	3,200 - 3500 [19]
M	2,943.47	2,924.18	$-\text{CH}_2-$ stretching	2,930.00 [14]
L	1,649.19	1,681.98	C=O stretching vibration	1,665.00 [14]
K	-	1,566.25	C=C stretch (Q)	1,567.87 [14]
J	-	1,504.53	C=N stretch (Q)	1,495.06 [3]
I	1,433.16	-	C-O-H band	1,429.00 [19]
H	1,329.00	-	C-H bending	1,342.00 [19]
G	-	1,303.92	C-N-C stretching vibration	1,297.59 [3]
F	1,238.34	1,249.91	C-H bending	1,243.04 [14]
E	-	1,138.04	N=Q=N stretching	1,138.88 [14]
D	1,095.60	-	C-O stretching	1,095.00 [21]
C	850.64	-	C-C stretching of PVA	856.00 [21]
B	-	813.99	N-H bonding	813 [3]
A	-	513.08	C-C out-of-plane bending vibration in benzenoid units	506.24 [3]

Energy dispersive x-ray (EDX)

After obtaining information on the FTIR characterization, the following characterization is a composition test using EDX [21] (**Figure 4**). The EDX analysis results for PVA nanofiber (**Figure 4(a)**) indicate the presence of C and O elements. This result differs significantly from the EDX analysis of PVA/PANI nanofiber (**Figure 4(b)**), which shows the presence of C, O and N elements. The presence of Nitrogen (N) is the characteristic feature of polyaniline ($\text{C}_6\text{H}_5(\text{NH}_2)_n$).

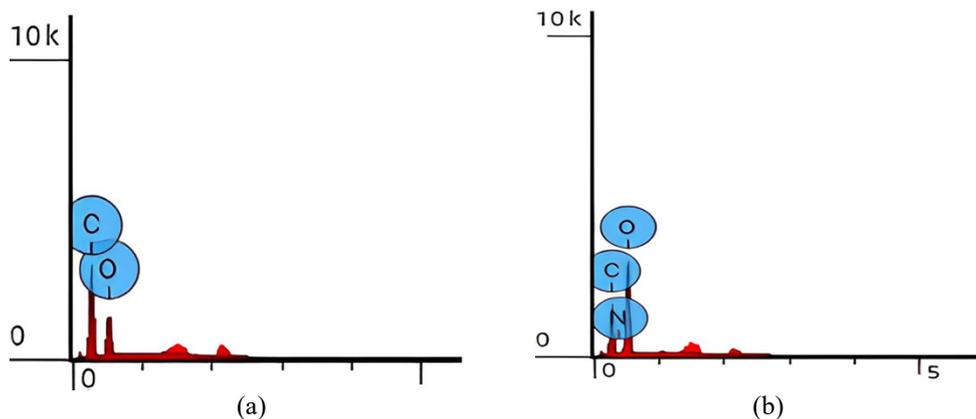


Figure 4 EDX composition test results (a) PVA and (b) PVA/PANI.

Optical microscope (OM)

The following characterization was morphological observation using an optical microscope (OM) at 100 times magnification. Observations with OM were carried out to determine the morphology of the electrospinning results with different PANI concentrations. We conducted the electrospinning in 2 concentrations (**Figure 5(a)**). Shows the PANI Electrospinning process for 2 h with PANI adding 1 g, which was carried out for 2 h. From this result, the PANI/PVA obtained thicker nanofibers (**Figure 5(b)**) shows the Electrospinning result for 2 h with 1.3 g PANI concentration, showing the fiber of PANI become increased and thicker from the previous concentration.

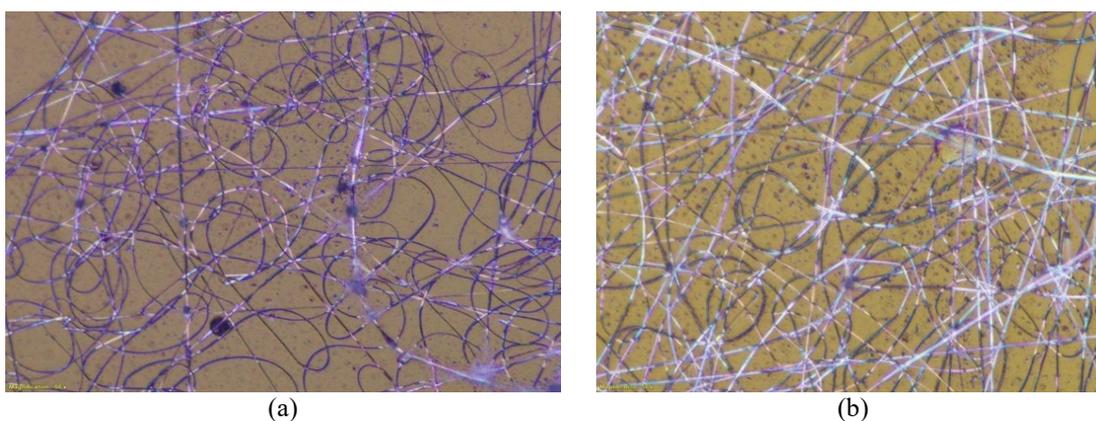


Figure 5 Results of morphological observations using an optical microscope for nanofibers (a) PVA/PANI_1_2 h and (b) PVA/PANI_1.3_2 h.

From the 2 results of morphological observations with OM, it can be seen that PANI powder (black particles) is visible in the electrospinning nanofibers. It confirmed that the electrospinning method has succeeded in synthesizing PVA/PANI nanofibers. The PVA polymer is white and looks silvery in the morphological observation results. These 2 types of polymer are significantly visible, and the results of these morphological observations strengthen the FTIR identification results discussed above. The results obtained based on observations using OM can be concluded that the concentration is related to the viscosity of the PVA/PANI solution, and this will affect the formation of fibers during the electrospinning process, and the time used also influences the amounts of formed fibers [22].

Scanning electron microscope (SEM) and porosity

The surface morphology of PVA and PVA/PANI nanofibers can be characterized using an optical microscope and a SEM. The sample particle size calculation is carried out after obtaining the best cross-sectional photo of the sample. After determining the best photo, the particle size can be determined using *Image-J* software.

Further morphological observations were carried out using SEM to obtain information on the diameter of the nanofibers from the electrospinning technique. The results of PVA electrospinning (**Figure 6(a)**)

show that the fibers formed are pretty thick. Fiber diameter was determined using *Image-J* software, with the average PVA fiber diameter being $0.3456 \mu\text{m}$. This diameter occurs because the PVA solution is liquid, so when it is fired, a lot of the PVA solution forms as fibers that stick to the collector.

In contrast, the PVA/PANI nanofiber resulting from electrospinning (**Figure 6(b)**) has a small average diameter, $0.313 \mu\text{m}$, and can be considered a nanofiber. A PVA/PANI solution containing 1 g of PANI powder is viscous. PANI is known to be quite difficult to dissolve in solvent. Adding PVA solution increases the solution thickness to improve the dissolvent ability significantly [23]. This ability is because the liquid flow from the syringe is very limited. So that only a small amount of liquid can stick to the collector during the electrospinning process. Thus, PVA/PANI nanofibers were obtained, which had diameters in the nanometer range following the objectives of this research.

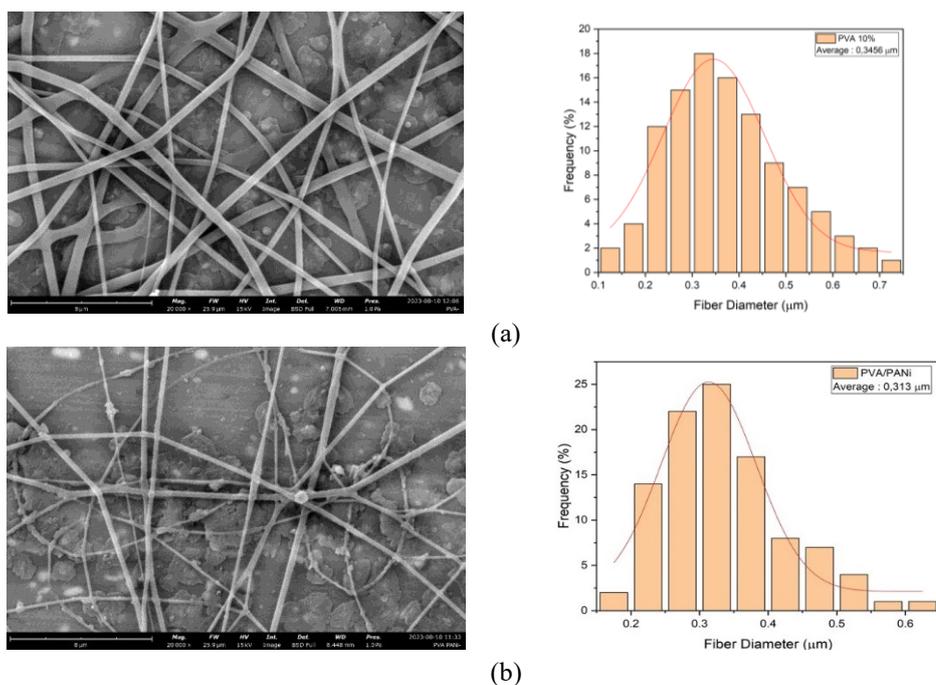


Figure 6 Results of morphological observations using SEM with $20,000\times$ magnification and nanofiber diameter measurements by *Image-J* software (a) PVA nanofiber and (b) PVA/PANI nanofiber.

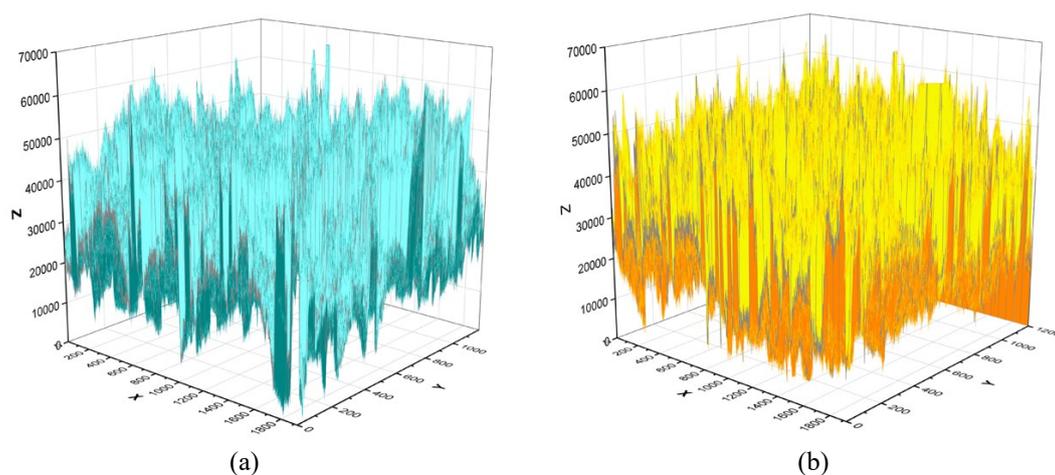


Figure 7 Nanofiber pore distribution of (a) PVA and (b) PVA/PANI (1 g, 2 h electrospinning).

The porosity of nanofiber is conducted to observe and measure the volume of voids or open spaces in a material or surface compared to the total volume of that material or surface [24]. **Figure 6** shows the porosity characteristic of PVA (**Figure 7(a)**) and PVA/PANI (**Figure 7(b)**). From the calculated data, the

porosity of PVA is 54.99 %, and PVA/PANI is 55.90 %. The bold color and light color from **Figure 7** show the porosity depth. The uneven distribution of sharpness occurs because of the Electrospinning process. Some fibers stack on each other, forming a layer of fibers. The percentage of porosity of PVA and PVA PANI shows the ability to absorb other materials.

Almost 54.99 % of PVA/PANI can absorb the material. In this case, the humidity level can be insulated on PVA/PANI properties. In other words, almost 55.90 % of the volume of the area owned will be filled by particles from outside. This result will affect the sensitivity of the sensor. PANI concentration electrospinning process can influence the porosity factor. The higher porosity will affect higher sensitivity [25]. Highly porous material surfaces will provide more surface area to interact with other materials (in this case, water molecules as humidity parameters). This porosity will lead to significant changes in electrical, chemical or mechanical properties that the sensor can detect. The results of the electrospinning process and the blending process of PVA with PANI will affect the viscosity of the resulting solution, and this can also influence the outcome of the formed fibers and the resulting porosity.

Four-point probe (FPP)

The characterization process includes the Four Points Probe (FPP) method [26], which assesses the performance of PVA/PANI nanofibers in response to varying relative humidity levels. The FPP method is employed to measure resistance changes resulting from humidity fluctuation. The humidity of an enclosed space is determined using silica gel and a saltwater solution. The humidity value ranges from 64 to 80 %. The humidity level below 64 % is unattainable in this study because Indonesia is a tropical country characterized by high humidity. This research performance was carried out within this humidity range. **Figure 8** indicates that variations of PANI powder content significantly impact the sensitivity performance of PVA/PANI nanofibers. When the nanofiber has a more significant PANI content, the change in resistance is significantly greater.

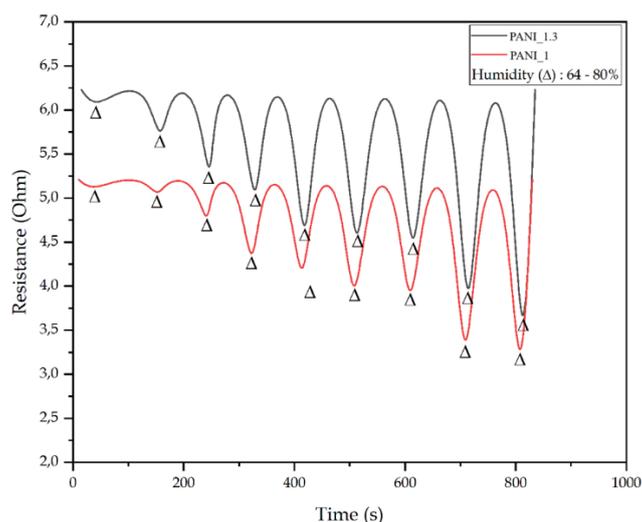


Figure 8 Performance test results of PVA/PANI nanofiber against room humidity.

Resistive humidity sensors are based on the principle that the electrical resistance of certain materials changes with humidity. As humidity levels change, the electrical resistance of this material changes proportionally. The change in resistance is used to calculate the relative humidity recorded by the FPP on the PVAPANI Sensor. **Figure 8** confirmed that the PVA/PANI sensor can measure relative humidity.

Sensitivity of PVA/PANI for humidity detection

Figure 9 indicates the relationship between humidity levels and sensitivity for 2 different PANI variant concentrations (1.3 and 1 g PANI). Both concentrations generally increase in line with the humidity level. This result suggests a positive correlation between humidity and sensitivity for the PANI concentration. The 1.3 g of PANI sensitivity appears to be consistently higher than 1 g. This data can be useful in demonstrating how humidity affects sensitivity for various PANI modifications. In this case, “Sensitivity 1.3_PANI” is higher than “Sensitivity 1_PANI,” which means “Sensitivity 1.3_PANI” is more sensitive at this humidity level.

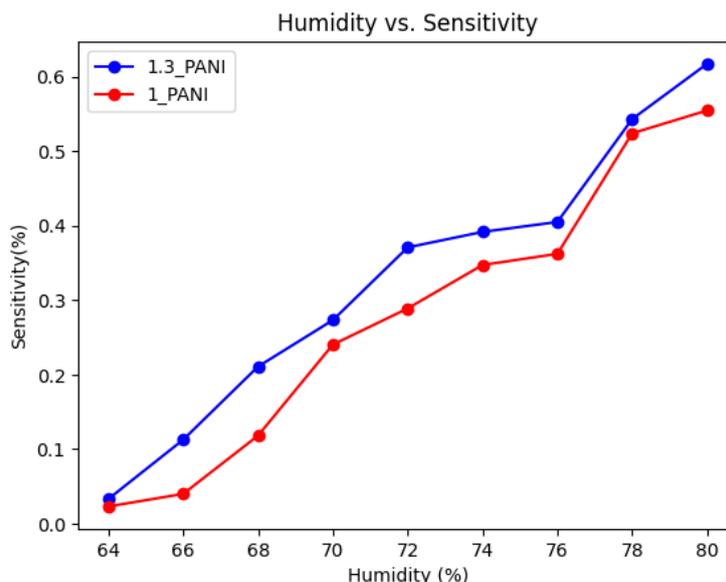


Figure 9 Relationship between humidity and sensitivity for 2 PANI variants.

This data can help demonstrate how humidity influences sensitivity to various PANI modifications in areas like materials research, sensor technology or environmental monitoring. The 1.3 PANI concentration is the maximum PANI added to the PVA solution for conditions where the viscosity can still produce fibers in the electrospinning method. Above this value, the resulting solution tends to be thicker and cannot produce nanofibers. If the concentration of PANI is below 1 g, the resistance is too high, and the conductivity is excellent to show significant resistance changes, making the sensor less sensitive. Small changes in resistance values cannot be measured effectively. This condition is related to the porosity, which is at 55 %. This porosity can capture water molecules within the PVA/PANI fibers.

Based on **Figure 9** regarding porosity, it will affect the sensitivity of PANI. The greater the porosity, the higher the sensitivity and vice versa. If the solution used is too viscous, it becomes challenging to form nanofibers and the porosity decreases, which is directly proportional to a decrease in sensitivity [25].

Conclusions

The optimal polymerization method was employed to produce nanofibers of polyaniline (PANI) through electrospinning, enhancing the material's conductivity and flexibility as an active sensor. PVA, a non-conductive polymer, was used in the nanofiber synthesis process on PANI. The synthesized PVA/PANI nanofibers were characterized using FTIR and EDX. Nanofibers have been formed from PVA/PANI synthesis of PVA/PANI nanofibers, with an average fiber size of approximately 0.313 μm . The porosity of nanofiber PVA/PANI is about 55 %, which is in line with the sensitivity. Higher porosity leads to increased sensitivity. Nanofiber PVA/PANI has the ability to measure humidity at 64 - 80 %. The FPP result shows that nanofiber PVA/PANI performed well as a humidity sensor and indicated resistance that changes in line with humidity in the environment. Adding PANI powder to PVA can produce nanofiber sensitive to humidity.

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