Conductivity Measurement of Nanostructured Film of PAA-PAN-Gold Nanoparticles

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***Abstract*— The effect of humidity on electrospun fibre morphology and conductivity on gold nanoparticles loading were investigated in the study. To produce nanoscale range of nanofibers and a consistent submicron size of fibres, electrospinning technique was introduced. Polymer blend of polyacrylic acid (PAA) and polyacrylonitrile (PAN) solution were used to form electrospun fibre. Mixture of PAA/PAN solution was used as precursor for the electrospinning. The distance from the tip of the needle to the aluminum foil plate for electrospinning, voltage, temperature and feed rate were kept constant. The humidity of the process was varied at 30%, 40%, 50% and 60% relative humidity (RH). 0.1 ml of gold nanoparticles (AuNPs) was used and added to the electrospun fibre. Then characterization analysis was done using SEM analysis and EIS analysis. Different humidity shows different morphology and different fibre size distribution. The average fibre diameter was the highest at 60% RH. Average fibre diameter increased as relative humidity increased and the fibre size distribution also increased as the relative humidity increased. Conductivity measured was the highest at 30% RH with the addition of AuNPs. AuNPs was an ideal material used to enhance conductivity.**

Keywords*— Electrospinning, Gold Nanoparticles (AuNPs), Nanostructured Film, Polyacrylic Acid (PAA), Polyacrylonitrile (PAN).

I. INTRODUCTION

Sensor fabrication technology is currently receiving a great interest among the researchers and the interest is expected to grow in the future. Sensors are well known to give information regarding our physical, chemical and biological environment. There are various types of sensors such as chemical sensors and biological sensors. One of the most important criteria for a sensor is that the sensor needs to be highly sensitive, quick response as well as recovery and low power usage to be consider as efficient and cost effective (Kumar et al., 2018). But majority of the sensors available in the market today operates at high temperature with poor sensitivity, selectivity and stability (Husain et al., 2018)

Polymers involving nanotechnology are being used in sensor technology to improve the sensor's performances as the chemical and physical properties of polymers can be alter based on various range of characteristics. The functions of polymers used in sensor devices are either they involve in the sensing mechanisms or they immobilize the components which responsible to detect the analyte (Adhikari & Majumdar, 2004). By replacing classical sensor materials with polymers and nanotechnology, a better selectivity and rapid measurements can be achieved. Polyacrylic acid (PAA) is regarded as an ideal sensing component because of its properties that has weak anionic polyelectrolyte (Ding et al., 2005). As for polyacrylonitrile (PAN), for the past 50 years, PAN fibrils have been referred by many researchers in their study. A research done by (Zhang et al., 2011), he constructed a theoretical ternary phase diagrams of H2O/DMFA/PAN to study the effects of H2O during wet spinning on the morphology of the PAN fibre. PAN was used in the research by (Zhang et al., 2011) because of its ability to form fibre, its chemical stability and also because of its anticorrosive properties.

In addition, nanoparticles also another material used that can enhance sensor performances. Significant properties of nanomaterials such as high surface area to volume ratio, improved chemical and optical properties have bring the sensor technology to another level in terms of their analytical performance. There are variety of metallic nanoparticles such as silver, gold, platinum and palladium nanoparticles available and are being exploited in order to improve the sensor performance (Mandal et al., 2018). Gold nanoparticles is among the most widely explored nanoparticles besides carbon nanotubes, because of its unique properties. AuNPs most usually being applied in the study of nanobiotechnology in term of their ideal property and variety of surface functionalities (R. Kafi, 2018).

Electrospinning is being introduced as a very suitable technique in order to produced nanoscale range of nanofibers. Its versatility in spinning various kind of polymeric fibers and to consistently produce a consistent submicron size of fibers are favorable as they are hard to achieve by other mechanical spinning techniques. As stated by (Deniz et al., 2011) in his research, in the last decade, electrospinning of functional nanofibres have gained a great attention as they produced very high surface area to volume ratio and this characteristic can be further improved by incorporating the nanofibers with additives such as nanoparticles. The range of fibres diameter formed is from less than 100 nm up to several microns (Frenot & Chronakis, 2003).

In spite of these advantages, a mixture of polyacrylic acid (PAA) and polyacrylonitrile (PAN) polymer solutions at weight ratio of 6:4 has been used as the precursor in electrospinning to produce nanostructured film. The objective of this research is to study the effect of humidity on electrospun fibre morphology and the effect of conductivity on gold nanoparticles (AuNPs) loading. The humidity of the process is being varied at 30%, 40%, 50% and 60% relative humidity and the other parameters are being kept fixed throughout the whole process to make it possible to study the effect of humidity on the electrospun fibre morphology by performing Scanning Electron Microscope (SEM) technique. AuNPs is loaded to each of the electrospun fibre at constant volume to increase the surface area as well as the conductivity measurement conducted by Electrochemical Impedance Spectroscopy (EIS) analysis.

II. METHODOLOGY

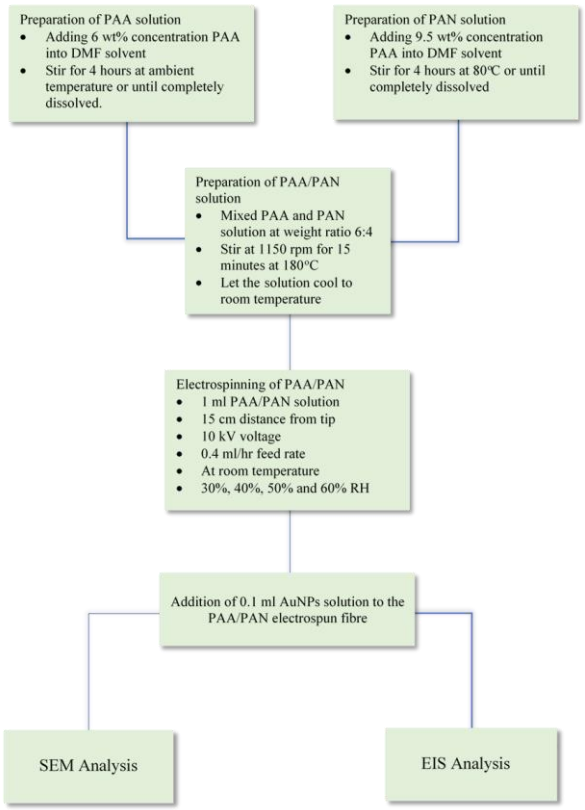


Fig. 1: Flow diagram of methodology

A. Preparation of Polyacrylic Acid (PAA) solution

Homogeneous solution of PAA was prepared by adding 6 wt% of 450 000 g/mol PAA into 44 ml DMF solution and was stirred gently using magnetic stirrer for 4 hours at ambient temperature (Li & Hsieh, 2005) or until completely dissolved.

B. Preparation of Polyacrylonitrile (PAN) solution

PAN solution was prepared by dissolving 9.5 wt% PAN powder with molecular weight of 230 000 g/mol into 44 ml of DMF solution. The solution was stirred using magnetic stirrer for 4 hours at temperature of 80°C (Liu et al., 2015) or until completely dissolved.

C. Preparation of polymer blend solution

PAA/PAN solution was prepared by mixing both PAA and PAN solution together at weight ratio of 6:4 (Liu et al., 2015). The polymer blend solution was stirred at 1150 rpm and 180°C for 15 minutes to ensure crosslinking of the polymers and let it cool down before being used in the electrospinning process.

D. Electrospinning process

A syringe with a needle of 1.5 mm diameter that was attached to it is being used. 1 ml of polymer blend solution, PAA/PAN, was filled in the syringe and the electrospinning was conducted at room temperature. The distance from the tip of the needle to the surface of working electrode of SPCE was set at 15 cm. The technique was performed at a voltage of 10 kV and at feed rate of 0.4 ml/hr (Beachley & Wen, 2009). The humidity of the process is being varied at 30%, 40%, 50% and 60% relative humidity. The electrospun fibre which were formed during the process as the product of electrospinning were then dried in desiccator for minimum of 12 hours to remove the solvent and then was heated in the oven for 30 minutes at 145°C.

E. Scanning Electron Microscope (SEM) analysis

Scanning Electron Microscope (SEM) was used to observe the morphology of the electrospun PAA/PAN fibre formed that was operated at 5kV. Elecrospun fibre were mounted directly on the SEM sample holder, then the micrographs of the selective areas were recorded at magnification of 4000. The sample surfaces are being coated with gold. The images obtained were analyzed and the average diameter of the fibre and fibre size distribution were determined by measuring (100 fibres) that were chosen randomly using Image J software.

F. Conductivity analysis

The conductivity analysis was conducted using Electrochemical Impedance Spectroscopy (EIS) to measure the conductivity of the electrospun fibre with and without AuNPs loading. For sample without AuNP loading, phosphate buffer saline solution was used to drop on the electrospun fibre that was formed on the DRP-C110 screen printed carbon electrode. For sample with AuNPs, 0.1 ml of gold nanoparticle (AuNPs) solution was loaded to each sample and dried before dropping the phosphate buffer saline. The readings were obtained and analyzed using Nova software which then being used to plot graphs for each relative humidity electrospun with and without the loading of AuNPs.

III. RESULTS AND DISCUSSION

A. Electrospun fibre characterization and fibre size distribution

For characterization of electrospun fibre, Scanning Electron Microscope (SEM) analysis was performed. **Fig. 2** shows the SEM images for 30%, 40%, 50% and 60% relative humidity together with the frequency graph of fibre size distribution. The SEM images shown in 4000 magnification. It was observed from SEM images obtained in **Fig. 2**, for 30% RH, the fibres arrangement were very packed and they had spindle-like structure as well as the electrospun fibres formed at 60% RH. Electrospun fibres formed at 40% and 50% RH are long-and-thin-like structure. A study by (An et al., 2018) stated that, it is expected to have slower solidification rate of jet as the humidity increased. It also caused the elongation and thinner diameter of electrospun fibre formed.

In **Fig. 2**, the average diameter of the fibre for 30% RH is 367 nm. The range of fibre size analyzed was around 200 to 600 nm with the highest distribution at 300 nm. At 40% and 50% RH, the average fibre diameter was 392 nm and 475 nm respectively which were thicker than fibre diameter at 30% RH. The frequency of fibre distribution for both 40% RH was the highest was at 300 nm and for 50% RH, the highest frequency of fibre size distribution was 400 nm. The average fibre diameter was the highest at 60% relative humidity which was about 668 nm, indicated that at this relative humidity, the electrospun fibre formed were relatively thicker compared to the lower humidity. This shows that as the humidity increases, the frequency of fibre size distribution also increases linearly (Parada et al., 2016).

The trend of fibre size distribution in **Fig. 2** was shifted from lower diameter distribution to higher diameter distribution. The frequency of the fibre at 30% RH were the highest at 300 nm and remain the highest distribution at 40% RH but the frequency was decreasing as the 400, 500 and 600 nm sized fibres were increasing. Moved on to the 50% RH, the highest frequency of fibre diameter was shifted to 400 nm where fibres of 700 nm had been measured at this humidity. Finally, the fibre size distribution was shifted three times to 700 nm at 60% RH and at this humidity, the diameter of electrospun fibres ranging from 300 to 1000 nm.

A study conducted by (Aghasiloo et al., 2019) stated that, at higher relative humidity, moisture content is also high. High water molecule affects the amount of excess charges on electrospun jet. This happened because of polarization of molecule. It might also cause decrease in the electric field intensity which considered as the main factor for jet elongation and whipping. High relative

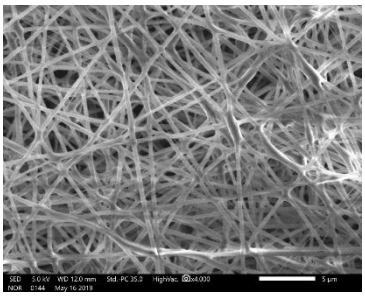
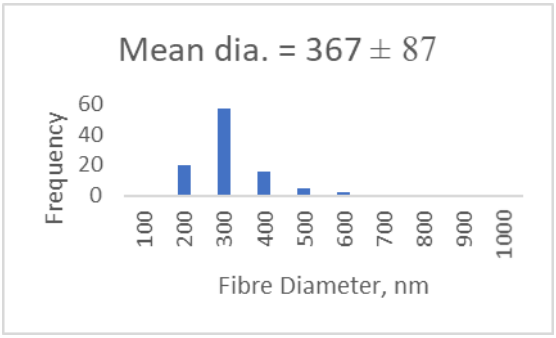
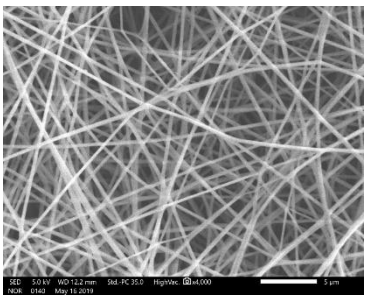
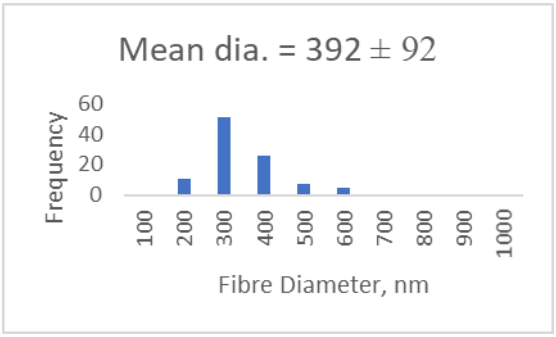
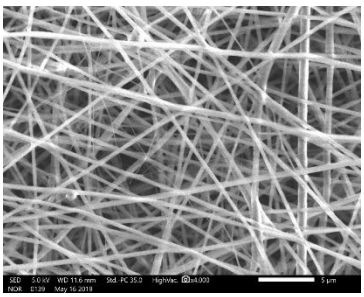
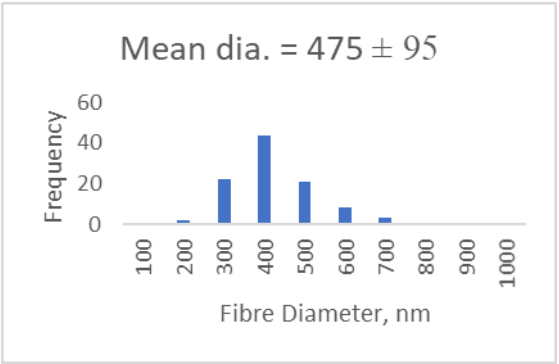
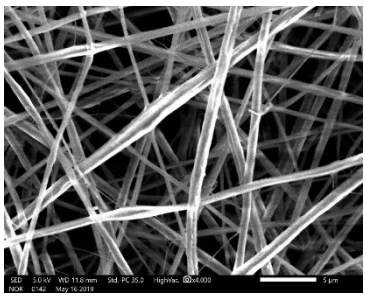
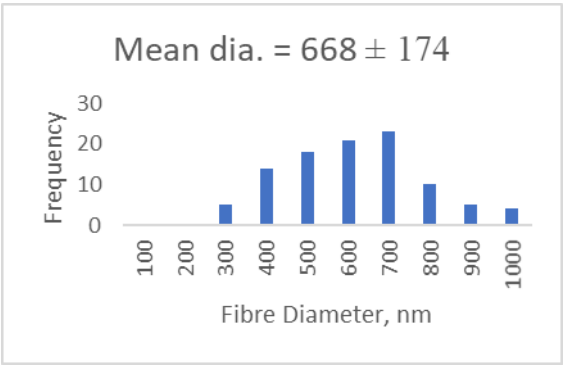
Relative Humidity	SEM Images	Size
30%		
40%		
50%		
60%		

Fig. 2: SEM images and fibre size distribution at 30%, 40%, 50% and 60% relative humidity

humidity led to a slow rate of evaporation and thus electrospun fibre cannot evaporate the solvent before it reached the plate (Bak et al., 2016). As the relative humidity increases, the high moisture content makes the fibre wet and could cause the fibre to diffuse with other fibres before drying (Liang et al., 2014).

A. Conductivity measurement of electrospun fibre

A Z' (Ω) versus -Z" (Ω) plot of the conductivity measured for four different relative humidity, 30%, 40%, 50% and 60% without gold nanoparticle loading was shown in **Fig. 3** and the graph of relative humidity with gold nanoparticle loading was shown in **Fig. 4.** The graph was plotted using the value obtained from EIS analysis.

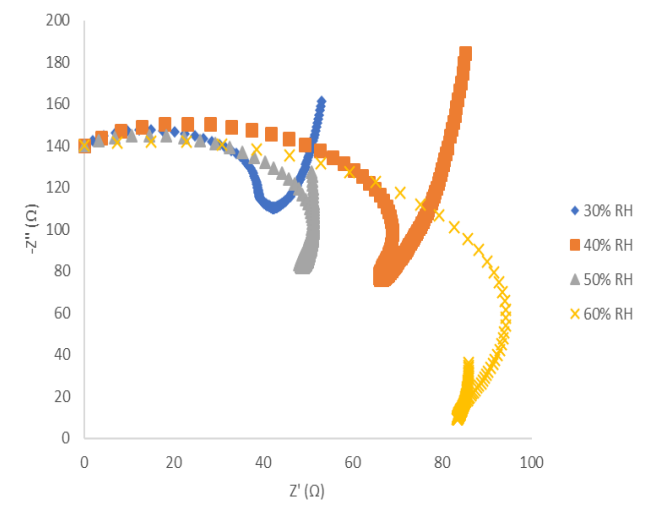


Fig. 3: Graph of relative humidity without AuNPs

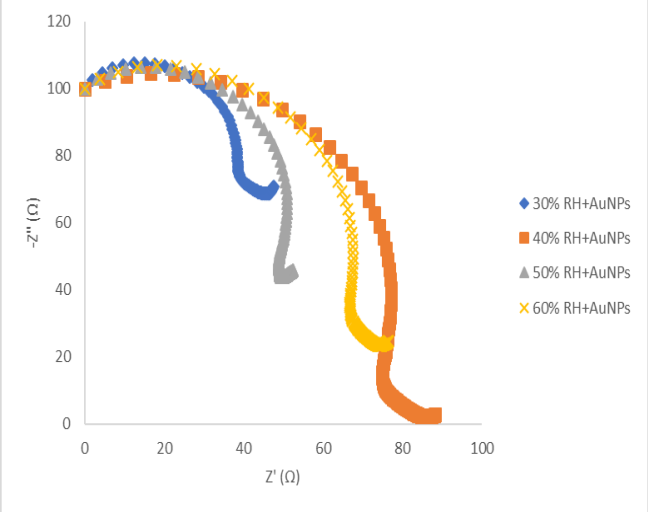


Fig. 4: Graph of relative humidity with AuNPs

Conductivity value were calculated using the equation (1) and the area was calculated using equation (2). The value of length, L, and area, A, were fixed. Value of bulk resistance, R_b was determined using graph plotted in **Fig. 3** and **Fig. 4**.

$$\sigma = \frac{L}{R_b A} \quad (1)$$

$$A = \pi r^2 \quad (2)$$

Table 1 shows the conductivity value calculated for relative humidity 30%, 40, 50 and 60%, with and without the loading of gold nanoparticles. The conductivity was the highest at 30% relative humidity that gave the value of 2.051×10^{-4}, followed by 50% relative humidity (1.654×10^{-4}) and 40% relative humidity (1.236×10^{-4}). Conductivity measured was the lowest at relative humidity of 60% with the conductivity value of 1.015×10^{-4}.

This shows that, in this research, the process conditions at lower relative humidity were more favorable to obtain a higher conductivity. While at higher relative humidity, the process conditions were not suitable enough to achieve a high value of conductivity.

Fig. 4 shows the graph of Z' (Ω) versus -Z" (Ω) plotted with the addition of gold nanoparticles (AuNPs) loading. AuNPs was used in order to increase the conductivity measured using EIS analysis. This is because, a study by (Mandal et al., 2018) stated that nanoparticles are materials used that can enhance sensor performances. So, in this study, AuNPs was used as nanoparticles to increase the conductivity in order to enhance sensor performance (Kizling et al., 2018).

Table 1: Conductivity value for different relative humidity

Relative Humidity	Without AuNPs		With AuNPs	
	Bulk Resistance, R_b	Conductivity, σ	Bulk Resistance, R_b	Conductivity, σ
30%	41.67	2.051×10^{-4}	40.00	2.137×10^{-4}
40%	69.17	1.236×10^{-4}	65.45	1.306×10^{-4}
50%	51.67	1.654×10^{-4}	46.36	1.844×10^{-4}
60%	84.17	1.015×10^{-4}	73.64	1.161×10^{-4}

From **Table** 1, the conductivity measured for 30% RH was the highest which was 2.137×10^{-4}. For 40% and 50% RH, the value of conductivity was 1.306×10^{-4} and 1.844×10^{-4} respectively. The lowest conductivity calculated was at 60% RH which was 1.161×10^{-4}.

The conductivity calculated for each relative humidity shows that the sample with AuNPs loading gave a higher value of conductivity compared to the sample without AuNPs loading. (Fritea et al., 2018) stated that, gold nanoparticles have high surface area, great conductivity and effective catalytic properties. It was suitable to be used as a conductivity enhancer in this study.

IV. CONCLUSION

The effect of relative humidity on electrospun fibre morphology that were formed by the method of electrospinning under constant process parameters were investigated. The fibre morphology were studied using the images obtained from SEM analysis. There was spindle-like structure formed at 30% RH. The average diameter of electrospun fibre ranging from 367 nm to 668 nm. The lowest average diameter was at 30% RH followed by 40%, 50% and 60% RH. A slower solidification rate of jet occurred as the humidity increased due to high moisture content makes the fibre wet and could cause the fibre to diffuse with other fibres before drying to form thicker fibre diameter. The frequency of the fibre size distribution were shifted from 300 nm to 700 nm as RH increased. Conductivity value measured the highest at 30% RH and the lowest at 60% RH for both with and without AuNPs loading. The addition of AuNPs to the electrospun fibres enhanced conductivity. The value of conductivity was higher with the addition of AuNPs compared to the electrospun fibres without AuNPs loading.

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