The Effect of Solution Concentration and Deposition Time on Viscoelasticity and Morphology of Polyaniline Coating

E I P Rahayu and N P Putri*
Physics Department, Faculty of Mathematics and Natural Sciences, Universitas Negeri Surabaya, Surabaya 60231, Indonesia

*E-mail: nugrahaniprimary@unesa.ac.id

Abstract. As one of the most studied conductive polymers, polyaniline (PANi) has a variety of applications, one of which is an active gas sensor, due to the presence of amine and imine groups in PANi that can easily react with gas. Quartz crystal microbalance (QCM) is a piezoelectric sensor with the working principle of frequency changes as a result of changes in mass on its surface. As an active gas sensor material on the QCM substrate, PANi must be deposited in the form of a thin layer. A good quality of thin film is if the film does not give loading the effect on QCM and has a homogeneous morphology. This research has succeeded in depositing PANi thin films by surface polymerization method by varying the parameters of PANi solution concentration and deposition time. Deposition parameters that are varied can be seen its effect on the viscoelasticity and morphology of PANi thin film formed. The viscoelasticity of the thin film was interpreted from the measurement of the thin layer impedance using an impedance analyser, while the morphology of the thin film was characterized using SEM. From the results of this study it was found that with the surface polymerization method, the PANi thin layer impedance value changes with the deposition time which is getting longer, but the change in impedance value is not significant and does not give a loading effect on QCM. At the same deposition time with different solution concentrations, the impedance value of the formed layer also does not give a loading effect on QCM. Although it has successfully deposited PANi with a surface polymerization method, the morphology of the PANi film formed is not yet homogeneous, as seen from the formation of PANi agglomeration on the QCM surface.

1. Introduction
Polyaniline (PANi) is a conductive polymer that has easily synthesized properties and has unique characteristics with electrical good conductivity and high stability [1]. PANi has considerable potential for a variety of applications including anti-corrosion coatings, sensors, batteries, electronic materials and other optoelectronic fields. Various PANi polymerization methods have been carried out before including oxidation [2], interfacial [3] and electrochemical [4]. In the oxidation and interfacial methods PANi produced in the form of powder. Polyaniline has been widely researched and used for sensor applications because it has good electrical conductivity, good environmental stability and is easily synthesized [5]. For PANi applications as active sensor material, PANi powder must be made in solution so that the appropriate solvent is needed. The solubility level of PANi to solvents is quite low so it is difficult to get a good and homogeneous PANi coating. While the
electropolymerization method requires more complex equipment to obtain a homogeneous PANi coating. As an alternative, we can use the direct coating method, surface polymerization [6]. This method is easier because it requires a relatively shorter time compared to other methods. synthesis is simpler, the PANi layer obtained has a dimensionless nano thickness and can increase PANi electrical conductivity.

Quartz Crystal Microbalance (QCM) is a biosensor that can detect the presence of a compound / molecule by changing the frequency of the quartz crystal resonator. The thickness and uniformity of the layers covering the QCM affect the sensitivity and stability of the QCM sensor. QCM is a piezoelectric material consisting of thin quartz crystal chips coated with silver electrodes on both sides. QCM has a unique resonant frequency and converts surface acoustic waves into electrical signals. If a chemically sensitive thin film on the QCM surface absorbs certain molecules, the mass of the layer will increase and cause a change in impedance to QCM. One of the strengths of this QCM sensor is that it can easily adjust various analyzes by applying different coatings. This makes QCM a versatile type of sensor [7]. This change in impedance can be detected with the help of an impedance counter (impedance analyzer) when an acoustic wave is converted into an electrical signal [8].

Sensors with PANi active material superimposed on the QCM surface have been proven to be effective in coating PANi using polystyrene on QCM with the spin coating method and thermal evaporation techniques being the method widely used in deposition techniques [9]. However, in this study using the direct method, namely the surface polymerization method, because this method is more effective, simple and does not require a long time.

2. Material and Method
The substrate used in this study was a Quartz Crystal Microbalance (QCM) silver electrode with a resonance frequency of 10MHz. QCM is a biosensor that has been proven effective in detecting compounds both in liquid and gas form. With the surface polymerization method, aniline and APS solutions are first mixed, then dripped on the QCM surface with different variations in molarity and time. Molarity variations used were 0.06 M; 0.08 M; and 0.1 M, while variations in deposition time are 20s, 40s and 60s.

The first step that must be done is to prepare 2 kinds of solutions, namely aniline + HCl 0.1 M and APS + HCl 0.1 M. Both solutions are then mixed and allowed to stand for 30 minutes / until the solution is mixed homogeneously and turns dark purple. The next dripping PANi solution in QCM by 1 μl and allowed to stand in accordance with the time varied. After PANi is deposited above QCM, then QCM is washed with 0.1 M HCl solution and dried in the oven for 30 minutes at 50°C. Then the impedance value will be measured using an impedance analyzer. Impedance analyzer is used to analyse the viscoelastic properties of the PANi layer so that loading can be detected in QCM. This measurement is carried out on QCM which has not been deposited and after deposition. To determine the morphology of the PANi layer, PANi characterization tests were performed, namely the Microscope Optic (MO) and Scanning Electron Microscope (SEM) tests. Thus, this study aims to find the optimum value of the synthesis parameters so we get the PANi thin film that does not have a loading effect on QCM.

3. Results and Discussion
3.1. FTIR result
FTIR characterization was used to identify the presence of polyaniline functional groups deposited by the surface polymerization methods. FTIR results can be seen in Fig 1, while the results of matching FTIR spectrum peaks with the results of previous studies can be seen in Table 1. From the results of spectrum peak matching, it is known that PANi has formed in the emeraldine (ES) salt phase event thought there are some shifting peaks, namely bond CH bending (Q) and C = N stretch (Q) [10]. However, the shift that occurred is not large so it can be said that this surface polymerization method has succeeded in synthesizing PANi.
Figure 1. FTIR Test Results of PANi samples with 0.06 M molarity

Table 1. Spectrum peaks of PANi

| No  | Wave number (cm⁻¹) | Bond type             |
|-----|-------------------|-----------------------|
|     | Data sheet | Reference | Surface Polymerization |                         |
| 1   | 1650-1560        | 1640.44 | 1612.49 | C=C stretch (Q)        |
| 2   | 1500-1400        | 1463.00 | 1365.6  | C=N stretch (Q)        |
| 3   | 1335-1250        | 1298.00 | 1338.60 | C-H bending (Q)        |
| 4   | 1250-1020        | 1224.55 | 1209.37 | C-N stretch,           |
|     |                   | 1124.18 | 1141.86 | C-C stretch,           |
|     |                   |           |          | C-H bending (B)        |
| 5   | 850-550          | 593.00  | 540.07  | C-H bending            |

3.2. Impedance Analyzer

Impedance measurement results from this study can be seen in Fig 2, where there are 3 variations of molarities namely 0.06M, 0.08M, 0.1M with each deposition time of 10s. The green colour curve is the result of QCM before coated with PANi, while the black colour curve is the measurement of impedance from QCM that has been coated with PANi with a molarity of 0.06 M. The red curve shows the measurement results of the impedance of QCM + PANi with a molarity of 0.08 M, and the orange curve shows the impedance measurement graph of QCM + PANi with a molarity of 0.1M. Impedance values that do not provide a loading effect if the impedance value does not exceed 100 Ω. Large impedance values can be caused by uneven coating surfaces, because the effects of loading that is too large can cause QCM to be overburdened and cannot function as a sensor.
Based on the graph of the relationship of frequency with impedance in Fig 2, it can be seen that the impedance curve at QCM before deposition has seen its peak decrease sharply, as well as the QCM impedance curve after being coated with PANi. There is a shift in the peak frequency towards the left with different widths on each curve. The frequency shift is due to molarity variations in the PANi solution so that the deposited mass also varies. It can be seen that at the same deposition time, the peak of the impedance curve that is closest to the initial impedance curve is at a concentration of 0.06 M, which has an impedance value of 24.212 Ω. From these results it can be concluded that a sample with a concentration of 0.06 M is the best sample seen from its impedance value. The highest impedance value is at 0.08 M molarity which is 64.925 Ω, although the end of the impedance curve is blunted when compared to the other two curves, with an impedance value less than 100 Ω, it can be said that the 0.08 M concentration still does not give a loading effect at QCM.

Figure 2. Relationship of frequency with QCM impedance values before and after PANi deposition with molarity variations.

Figure 3. Frequency relationship with QCM impedance values before deposition, and after deposition of PANi solutions with time variations.
Fig 3. shows the QCM/PANi impedance curve at a concentration of 0.06M with different deposition time variations, i.e. 20 s, 40 s, and 60 s. The green curve is the QCM impedance value before coated by PANi, the black curve is the QCM impedance value that has been coated by PANi for 20 s, the red curve is the QCM impedance value that has been coated by PANi for 40 s and the orange curve is the QCM impedance value that has been coated with PANi for the 60 s. There was a significant shift in the peak of the curve at the deposition time of 20 s and 40 s, whereas for deposition time the 60 s almost overlapped with the initial QCM impedance curve. The peak of the curve with a time of 20 s looks more blunt when compared to other curves. It is because the time of 20 s is the shortest deposition time. The PANi polymerization process is getting more perfect by longer deposition time because when washing is done, the PANi powder has deposited on QCM surface. While if the deposition time is faster, the PANi solution gives little effect loading on QCM so the polymerization process has not run perfectly, so the PANi solution has little effect loading on QCM. Nevertheless, the impedance measurement shows that even though time variation is carried out, the result of the impedance value still does not give a loading effect on QCM.

3.3. Microscope Optic (MO)
Optical Microscope characterization was carried out to observe the morphology of the PANi layer formed on the QCM surface. The results of observations can be seen in Fig 4. The picture shows that the PANi layer is not evenly distributed in all deposited parts. This is shown at the black dots scattered in several parts, and there are still clumps (agglomeration) on the deposited surface.

![Figure 4. PANi coating optical microscope results above the QCM surface with a molarity of 0.06 M](image)

3.4. SEM
Fig 5. shows the morphological results of the PANi layer above QCM at a molarity of 0.1M. In the picture below, it can be seen that the PANi layer formed has not been homogeneous, the PANi agglomeration is still forming in QCM, and the white colour is lumpy in the middle. While the black striped is an electrode from QCM. The results of PANi morphology with molarity of 0.1 M although agglomeration is still visible because the PANi coating formed is not yet homogeneous, but the results of impedance at the 0.1 M molarity are still below 100 Ω and the loading does not occur.
Figure 5. SEM results with 2000 times magnification on the surface QCM coated PANi with molarity of 0.1 M

4. Conclusion
This research has succeeded in deposition of the polyaniline layer above QCM with the surface polymerization method. Variations in molarity and deposition time did not affect the viscoelastic nature of QCM and did not provide a loading effect on QCM. However, with this method the morphology of polyaniline is not yet homogeneous and agglomeration is still formed.

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