Solvent Effect on Viscoelastic Behaviour and Morphology of Polyaniline Coating at QCM Sensor

N P Putri¹, D W Pravitasari², F A Iz Al Aziz², Maulidiah², D J D H Santjojo², Masruroh²*, and S P Sakti²
¹Physics Department, Universitas Negeri Surabaya, Surabaya, Indonesia
²Physics Department, Brawijaya University, Malang, Indonesia
*e-mail: ruroh@ub.ac.id

Abstract. The effect of different solvents and solution concentration on viscoelastic behaviour and morphology of polyaniline (PANI) coating was investigated in this study. The PANi coating on a QCM sensor was created by spin coating with various solvents, such as NMP, m-cresol, and DMF with varying concentrations of 1-4% by weight of PANi. The viscoelastic behaviour was observed by impedance analyser and morphology of the PANi coating was observed via optical microscope and SEM/EDX. The viscoelasticity was measured to determine whether the coating produces an acoustic load (loading effect). The observations showed that the different solvents give a different effect on the impedance value of the PANi coating. With m-cresol solvent, the impedance value in the series resonant frequency was so large, indicating the PANi coating was not rigid and produce a loading effect on QCM sensor. From morphology observation showed that homogeneity of the polyaniline coating is still poor. There is an agglomeration of polyaniline powder which is insoluble in the solvent used. From the viscoelastic properties of the coating, the optimum value was obtained in PANi coating with NMP solvent.

1. Introduction
Quartz crystal microbalance (QCM) is one of the piezoelectric sensors that allow selective detection of biological events in real-time. This sensor has a working principle based on changes in the oscillation frequency which is proportional to the changes in the deposited mass. QCM is the most widely used acoustic resonator device because it allows the study of viscoelastic properties of materials, molecular adsorbs and living cell mobility. The Saurbrey equation assumes that the mass or film deposited on the QCM surface will follow the QCM vibration and therefore the coated QCM will only behave as if it were thicker. The effective wavelength of the crystal will increase and cause the resonance frequency to decrease. This model assumes that there is no energy dissipation and thus only applies to thin, rigid and homogeneous films and has the same acoustic properties as QCM materials. QCM can function as a sensor if the deposited mass does not have a viscoelastic effect so that QCM does not have a damping experience. The sensitivity and selectivity of QCM can be adjusted to the selection of the right chemo sensitive film.

Conductive polymers for example, polypyrrole, polythioene, and polyaniline, have been used as sensors for hydrocarbon gas sensors, CO, NOx, and organic vapors [1]. With low operating temperatures, conductive polymers are better candidates for sensor materials than metal oxide-based
sensors. Among the types of conductive polymers, polyaniline (PANi) is one of the materials that are in great demand because it has several superior features, including being easily polymerized, has good redox reversibility, and has good environmental resistance. Polyaniline has been proven to be an active gas sensor that can detect a variety of gases for example, alcohol [2], chloroform [3], free radicals [4], hydrocarbons [5] and scents [6].

To form a polyaniline thin film on the QCM surface, several deposition methods can be carried out, one of which is the spin coating method. Spin coating is a procedure used to apply a uniform thin film to flat substrates. This method is very easy and has been proven to form a homogeneous thin film. Several factors influence the quality of the thin film formed using the spin coating method, including the spin coater rotational speed, solvent selection and the solution’s concentration [7]. Spin coater rotational speed will affect the deposited film thickness which will also affect the thin film sensitivity. However, a thick film will give the loading effect on QCM, so that the optimal rotating speed is needed where the thin film formed will not give the loading effect. Several solvents can be used to dissolve polyaniline. The physical and chemical properties of each solvent can be used as a reference for choosing a solvent that is adjusted to the use of thin film. The concentration of the deposited solution on the surface of QCM will influence the morphology of thin film formed. The thin film formed is expected to have porous morphology so that it is suitable when functioning as a sensor.

In this research, a PANi deposition was carried out on the QCM substrate using the spin coating method. Spin coating deposition parameter variations were performed, namely variations in the type of solvent, solution concentration, and rotational speed. The effect of deposition factors of spin coating method on viscoelastic properties and morphology of the PANi thin film deposited on QCM surface was explored. The viscoelastic properties of thin film were analysed from changes in the impedance values due to variations in rotational speed, type of solvent, and solution’s concentration, while the morphology and microstructure of the film were analysed based on the results of Optical Microscope and Scanning Electron Microscope (SEM).

2. Experimental Procedures
2.1 Synthesis of polyaniline solution
To make a polyaniline solution, polyaniline (PANi) powder must be synthesized first. The synthesis of PANi uses the oxidation method as has been done in previous studies [8]. The oxidized polyaniline powder was then dried and crushed with mortar until a fine powder was obtained with granules that could escape in the 325-mesh filter. The powder passed through the filter was then dissolved with a variety of solvents, namely N-Methylpyrolidine (NMP), m-cresol, and N.N-dimethylformamide (DMF). The concentration of the solution is also varied, which is 1 - 4% by weight of PANi. Making the solution using a magnetic stirrer with a speed of 1500 rpm for 2 hours, then continued with ultrasonication for 2 hours to obtain a homogeneous solution. After obtaining a homogeneous solution, the solution is then dropped over the surface of the QCM and rotated with a variety of rotational speed 1000- 4000 rpm for 60 seconds. The coated QCM then dried in an oven at temperature 100˚C for 10 minutes.

2.2 Characterization
Before and after coated with PANi, the impedance value of QCM was measured using an impedance analyser to see changes in the QCM viscoelastic properties due to PANi deposition. The morphology of the PANi coating was analysed using an optical microscope and Scanning Electron Microscope (SEM). Energy Dispersive X-Ray Spectroscopy (EDX) is used to identify elements in the polyaniline film deposited above QCM.

3. Result
3.1 Variation of solvent
The deposition process of PANi on the QCM surface by spin coating method requires the presence of a homogeneous solution, so the role of the solvent is very important in this method. Because PANi is
one of the polymers that have low solubility in organic solvents, the selection of the right solvent must be done first by considering their solubility parameters. The solubility parameter can be used to predicting polymer solubility. The basis of these so-called Hansen solubility parameters (HSP) is that the total energy of the vaporization of a liquid consists of several individual parts. These arise from dispersion forces (d), permanent dipole forces (p) and molecular hydrogen bonding (h) [9]. The overall solubility parameter can be calculated by:

\[ \delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \]  

(1)

From the above equation, it was found that the solubility parameter value of m-cresol was 11.11 MPA\(^{1/2}\), NMP was 21.48 MPA\(^{1/2}\), and DMF was 12.14 MPA\(^{1/2}\) [10]. Thus, PANi will dissolve faster in NMP solvents because the solubility coefficient is the greatest among other solvents. The solubility parameter (\(\delta\)) is directly proportional to the solvent evaporation energy (\(\Delta E_{\text{vap}}\)) and inversely proportional to the mean molar volume (\(V_m\)). Evaporation energy will correlate with solvents vapor pressure which will affect the morphology of the deposited polymer on the QCM surface.

Quartz Crystal Microbalance response measurement can be done using a frequency measurement, dissipation signal and also impedance measurement. Among many methods, the electrical impedance is one of the preferred analyses. The impedance measurement can lead us to investigate the material properties, such as complex shear modulus, viscosity and loading effect caused by coatings on QCM’s surface [11]. In this study, impedance measurements were carried out on QCM before and after PANi coated to analyse loading effect obtained by QCM due to the solvents used. It was found that the deposition of PANi with various solvents gave a different loading effect on QCM (Figure 1).

![Figure 1](image)

**Figure 1.** Frequency changes in QCM due to PANi coating with various solvents (a) NMP, (b) m-cresol, and (c) DMF
From the impedance-frequency graph in Figure 1, a minimum impedance value identifies the series resonant frequency, and the maximum impedance value identifies a parallel resonant frequency [12]. The measurement result showed that the series resonant increased, indicating a change in impedance value. From the shift, we can see that PANi coating shows different viscoelasticity, which causes significant differences in the impedance value as a result of various solvent. Solution or analyte sorption not only increases the mass of the coating (mass effect) but also changes the shear parameters of PANi (viscoelastic effect) [13]. The biggest frequency shift value is owned by m-cresol solvent, whereas for NMP and DMF solvents the frequency shift that occurs is not too significant (Table 1). M-cresol is a PANi solvent which can increase PANi conductivity by secondary doping. M-cresol is also hygroscopic, so it can react with water vapor in the environment. The interaction between PANi and m-cresol and water vapor causes an increase in mass deposited on QCM’s surface. Different solvents can provide different viscoelastic effect, this can be seen from the change in measured impedance value (increase in the minimum curve peak). From the impedance change data in Table 1, it can be seen that m-cresol also gives a large viscoelastic effect on PANi. Changes in the viscoelastic properties of PANi due to m-cresol solvents cause QCM to get a loading effect so that it cannot function as a good sensor.

| Solvent | Frequency changes (Hz) | Impedance changes (Ω) |
|---------|------------------------|-----------------------|
| NMP     | 1841,333               | 49,119                |
| m-cresol| 3904,762               | 169,018               |
| DMF     | 1333,333               | 76,716                |

3.2 Variation of the solution’s concentration
Impedance measurement data with variations in solvent and concentration can be seen in the graph in Figure 2. A good impedance value is a small one, which is related to the viscoelastic nature of the thin film formed above QCM. If the PANi film impedance value is too large (> 100Ω), then it can be said that the PANi film formed is rubbery, otherwise, if the PANi film's impedance value <100Ω, then the film is still rigid. It can be seen that the optimum impedance value is obtained at the PANi film derived from NMP and DMF solutions at 2% concentration. In all samples, films with concentrations other than 2% have a greater impedance value. In a solution with a concentration of 1%, there is a small amount of PANi powder, so that when the spin coating process is carried out, there will be an interaction between the solvent (which has a greater concentration) with QCM which results in a loading effect. QCM drying process after spin coating cannot completely remove the solvent (trapping process occurs). On the other hand, in solutions with concentrations greater than 2%, more dissolved PANi powder, so that it will add deposited mass to the QCM surface which results in an added loading effect on QCM.
Figure 2. The impedance value of the PANi coating with various solvent and solution concentration.

The surface morphology of PANi coating is shown in Figure 3. All the images correspond to coating with PANi in the NMP solvent. There is a difference in dispersion between the PANi films at different solution concentrations. Coating derived from 2% PANi solution in NMP solvents (Figure 3.a) have better morphology, showing a more even dispersion compared to the second film (Figure 3.b). This morphology is directly related to solution concentration. As explained above, that with different concentrations of solution, the amount of PANi powder dispersed in the solution is also different. So that the solution with a concentration of 4% has more PANi powder content when compared to a solution with a concentration of 2%. With the increasing number of PANi powder in the solution will reduce its solubility, so that during the spin coating process, many PANi powders will clot and form agglomeration on the QCM surface. This will obviously affect the PANi layer impedance value. From the impedance measurement data (Figure 2), it can be seen that the value of the impedance of the coating coming from the solution with a concentration of 4% has a very large impedance. So, it can be concluded that the agglomeration of PANi powder gives a greater loading effect on QCM. PANi prepared by oxidation with HCl doping has properties that are not easily soluble to organic solvents, so the right solution concentration is needed so that PANi particles can be dispersed properly.

Figure 3. Observation of PANi layer morphology using an optical microscope (100x magnification) with variations in the concentration (a) 2% and (b) 4%
3.3 Variation of rotational speed

The effect of spin coating rotational speed on the viscoelastic properties of the PANi coating can be seen in Figure 4. It can be seen that the spin coater's rotational speed greatly affects the thickness of the film which has an impact on the magnitude of the PANi coating impedance value. The optimum value is obtained in the sample rotated at 4000 rpm. When the rotating speed is low, thicker films will be produced compared to high rotating speeds. With a high rotating speed, the films formed will be thinner and not burden QCM. PANi solution with 2% NMP solvent dripped on the QCM surface will be distributed evenly because of the centrifugal force so that the film will experience thinning during the spinning process.

![Figure 4. The impedance value of the PANi coating with variations in rotational speed](image)

Rotational speed variations also affect the morphology of the PANi coating formed (Figure 5). At 1000 rpm rotation speed, there are islands of PANi particles in the formed coating. This can occur because when the rotating speed used is low, the process of spreading the solution is slow so that the formed film is not uniform and agglomeration occurs. On the contrary, with a high rotational speed, the centrifugal force on the spin coating turns greater and forcing the film to spread faster, this causes fewer agglomerations.

![Figure 5. Morphology of PANi coating in 2% NMP with the rotational speed of (a) 1000 rpm and (b) 4000 rpm](image)
3.4 Microstructure

The morphology of the PANi coating with DMF 2% solvent can be seen in Figure 6. The effect of the solvent on the film morphology can be explained by the value of the vapor pressure of each solvent, as mentioned in the initial part of the discussion. Vapor pressure value at 20°C for NMP solvent is 31.6 Pa, while m-cresol is 18.6 Pa and DMF has a vapor pressure of 380 Pa. From the value of the vapour pressure of each solvent it can be seen that DMF is very volatile, much faster than the other two solvents. Solvents that rapidly evaporate can result in the dissolution of the dissolved PANi, as can be seen in Figure 6. The morphology of the PANi coating above the QCM surface is still not homogeneous, there are still many PANi powder which is agglomerated and do not spread evenly. This can result in an uneven distribution of stress, which increases the viscoelasticity of QCM.

PANi powder which is deposited on the QCM surface has a spherical shape and nanometre dimension, it can be seen that the powder diameter is in the range of 70-80 nm. PANi powder dissolving process in each solvent has several stages, namely, starting with grinding to pass the filter until stirred with a magnetic stirrer for 2 hours and ultrasonied for 2 hours as well. This process can reduce the size of the PANi powder to nano dimensions.

![Figure 6. Morphology of PANi coating in 2%DMF at QCM surface](image)

From the EDS analysis (Figure 7) it can be seen that the most deposited element on the QCM surface is carbon (C) of 77.50 %wt and oxygen (O) of 13.58%wt. This proves the existence of PANi which has a molecular formula (C₆H₄NH)n on the QCM surface. The presence of Cl element (1.51 %wt) is due to the polymerization process of PANi which uses HCl, while the Ag element is the electrode on QCM. Ag elements still detected in EDS spectra show that the silver electrodes in QCM have not all been coated by PANi.
4. Conclusion

From this study it can be concluded that to form a thin film of PANi on the surface of QCM using the spin coating method, the recommended solvent is NMP with a solution concentration of 2% and rotational speed of spin coating of 4000 rpm. It has been investigated that with a 2% PANi-NMP solution the film formed does not give a loading effect on QCM so that it can still be used as a sensor.

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