Synthesis of polyaniline/cellulose composite as humidity sensor

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Abstract. Water hyacinth is one weed plant that has cellulose content of 60% on the stem and is a good absorbent. In this study cellulose extraction from hyacinth has been done through several stages. Polyaniline/cellulose composite (PANi/cellulose) is prepared by an in-situ chemical method using cupric sulphate as an initiator. The representative PANi/cellulose samples are characterized by Fourier Transform Infrared (FTIR). On comparing it appears that spectra PANi/cellulose contains vibrational bands due to both PANi and cellulose. This may indicate the formation of PANi/cellulose composite. From the resistance measurement results, it can be seen that with the addition of cellulose to PANi can improve the sensitivity of the polyaniline based moisture sensor

1. Introduction
Humidity can affect the chemical, physical and biological process that occurs in everyday life. For example, food and medicines stored in a container require a certain level of moisture in order not to break down quickly. Human comfort is also influenced by humidity somewhere. Humans will feel less comfortable in places with high humidity because the high humidity will trigger the breeding of microorganisms that carry disease germs. However, low humidity (less than 20%) will also cause drying of membrane mucous membranes, therefore the human body needs an environment with sufficient moisture levels. Commercially available humidity sensors are fabricated by conventional sensing materials like ceramics [1] and electrolytic metal oxides. Organic materials due to light weight, flexibility, low cost and large surface area have developed the great interest for their use in humidity sensors. The humidity sensors based on organic sensing materials are classified into capacitive, resistive, optic [2], mechanical, and thermoelectric type of sensors depending on basic sensing principle [3].

Polyaniline is one of the most widely applied conductive polymers due to its highly regulated, stable and easily produced. The use of polyaniline as a humidity sensor has been carried out by previous researchers. L. Qianqian et.al which synthesize polyaniline nanofiber to be used as a sensor for pavement. From this research, it is found that nanofiber polyaniline can be applied to good humidity sensor, and its sensitivity increases with the addition of PEO which is hydrophilic [4]. Milind V.K, et al also uses polyaniline as a humidity sensor by ink-printed technique to obtain a flexible humidity sensor [5]. Pablo Cavallo et.al report the mechanism of resistivity changes on humidity sensors made by polyaniline [6].
Cellulose is one of the biopolymers found in plants, such as water hyacinth, which has cellulose content of 60% on its stem [7]. One of the most common characteristics of cellulose is hydrophilicity which is an important property to develop humidity sensors due to better adsorption sites for $\text{H}_2\text{O}$ molecules [8]. The present study reports the grafting of cellulose onto polyaniline chain to improve its adsorption. The electrical resistance of PANi-cellulose film on PCB substrate was monitored under controlled humid environment to explore its use for the humidity sensor.

2. Experimental Procedures

2.1. Extraction of cellulose
Cellulose extraction from water hyacinth consists of several stages, the first stage cleaning and drying stem of water hyacinth. A dried water hyacinth then cut, blended and sieved to obtain a homogeneous fibre size. The second stage is the dewaxing process using soxhlet apparatus. The result of the dewaxing process then soaked with NaClO$_2$ and allowed to stand for 3 hours in a water bath at 80°C. This process repeated up to 2 times then washed with distilled water. The next step is a process of hemicellulose removal, where the precipitate reacted with NaOH and soaked in the water bath for 4 hours. Thereafter, the precipitate was immersed in the NaClO$_2$ solution for 3 hours. To obtain pure cellulose fibre, the precipitate was immersed in NaOH for 4 hours at 60°C. Pure cellulose fibres soaking results then filtered and washed and then dried in the sunlight for 2 days.

2.2. Polymerization of Polyaniline (PANi)
Polyaniline was obtained by the chemical oxidative polymerization process. The oxidative polymerization reaction of aniline occurred by adding oxidant monomers like ammonium persulfate (APS) to aniline dissolved in an acid solution. For the aniline aqueous solution, 1.82 ml aniline was dissolved in 50 ml of 1 M HCl doping acid. For the oxidant solution, APS (5.71 gr) was dissolved in 50 ml of 1 M HCl doping acid. The oxidant solution was quickly poured into the aniline solution at room temperature followed by immediate magnetic stirring. The stirring was stopped after 2 h, and the solution left undisturbed for 24 h. The green precipitates were filtrate with filler paper and wash with distilled water. The product was finally dried out for FTIR characterization.

2.3. Synthesis of PANi/cellulose composite
Aniline (1.82 ml) and cellulose (0.3; 0.4; 0.5 g) were dissolved in 50 ml of 1 M HCl solution. For the oxidant solution, APS (5.71 gr) was dissolved in 50 ml of 1 M HCl doping acid. The oxidant solution was then quickly poured into the aniline solution at room temperature followed by immediate magnetic stirring. In resultant solution, 5 ml 1 M CuSO$_4$ was slowly added with continuous stirring for 1 h. The resultant solution was then left for 3 – 4 h and a dark-green precipitate was obtained. The precipitate was filtered then washed with distilled water and dried for characterization.

2.4. Characterization
FTIR spectra were recorded with Shimadzu FTIR spectrometer. Change in resistance of PANi/cellulose was measured with CD800a Sunwa digital multimeter. In order to evaluate the humidity-sensing behaviour of PANi/cellulose, a film was coated on PCB surface by spin coating technique after making 3% solution of PANi/cellulose in m-cressol.

3. Result

3.1. Spectra study
FTIR spectra of PANi, cellulose and PANi/cellulose composite are shown in Figure 1. Polymerization of PANi has been successfully performed in emeraldine salts (ES) form, which has quinoid and benzenoid groups which are characteristic of polyaniline (Table 1). Cellulose extracted from water hyacinth has the -O- bond which is one of the characteristic attributes of cellulose, so it can be
concluded that water hyacinth is one of the cellulose sources found in nature. On comparing it appears that spectra PANi/cellulose contains vibrational bands due to both PANi and cellulose. Further, the peak appeared in PANi spectra at 1640 cm\(^{-1}\) shifted at 1637 cm\(^{-1}\) in the composite. Otherwise, IR peak of cellulose appearing in spectra at 1317 cm\(^{-1}\) and 1157 cm\(^{-1}\) shifted at 1315 cm\(^{-1}\) and 1155 cm\(^{-1}\) in PANi/cellulose composite. These may indicate the formation of PANi/cellulose composite [8].

Table 1. Bond type for PANi, cellulose and PANi/cellulose.

| No  | Wave number (cm\(^{-1}\)) | PANi     | Cellulose  | PANi/Cellulose | Bond type                      |
|-----|-----------------------------|----------|------------|----------------|--------------------------------|
| 1   | 1650-1560                   | 1640.44  | 1621,52    | 1636,91        | C=C stretch (Q)                |
| 2   | 1500-1400                   | 1463.00  | -          | -              | C=N stretch (Q),               |
| 3   | 1400-1300                   | -        | 1316,60    | 1315           | O- bonding                     |
| 4   | 1335-1250                   | 1298.00  | -          | -              | C-H bending (Q)                |
| 5   | 1250-1020                   | 1224.55  | 1157,28    | 1155           | C-N stretch,                   |
|     |                              | 1124.18  | -          | 1020,21        | C-C stretch,                   |
|     |                              |          |            |                | C-H bending (B)                |
| 6   | 850-550                     | 593.00   | -          | 551,93         | C-H bending                    |

3.2. Humidity sensing behaviour

The measurement of humidity sensing behaviour is done in a confined space with a saturated salt solution [9]. The variation in resistance of PANi, cellulose and PANi/cellulose with an increase in humidity is shown in Figure 2. The higher the relative humidity percentage, the lower the resistance value obtained. This indicates there is an interaction between the PANi/cellulose film with the moisture content in the air. With increasing moisture in the air, more water molecules are absorbed to
the film surface (swelling effect). The water molecules bonded in the film will be ionized into H⁺ and OH⁻ ions. This will decreases the resistivity of the film [8]. In this study, the electrical resistance of the film decrease can be caused by the pores, initially filled with dry air, are progressively filled with water which has a higher dielectric constant than air, although there is no supportive morphological data.

From Figure 2 it can be seen that there is a decrease in PANi resistivity, from 1320 Ω (at 64% RH) to 100 Ω (at 80% RH) and has a good linearity. Cellulose is an insulator material that has much greater resistance when compared with polyaniline (4520 Ω at 64% RH). A decrease in resistance can be caused by an increase in water molecules binding to the -O- group on cellulose. With the addition of varying cellulose, it can be seen that the more cellulose is added, the lower the resistivity of the PANi/cellulose composite (when measured at 64% RH). With increasing humidity, the decrease in resistance is no longer linear but forms a polynomial curve. From humidity measurements of 64% to 69%, a decrease in resistance is very far when compared to humidity measurements at other points. Decreasing resistance at humidity measurements from 74% to 80% RH is lower than other points, since saturation has occurred, where the water molecules attached to the sample have reached the maximum. Grafted cellulose that has strong hygroscopic properties will improve the hydrophilic properties of PANi. The more cellulose that is grafted onto the PANi the more matrix as the absorbent of water vapour molecules. This may cause decreased resistivity of PANi/cellulose.

![Figure 2](image)

**Figure 2.** Change in resistance of PANi, cellulose and PANi/cellulose composite.

4. Conclusion

From this research can be concluded that cellulose has been successfully grafted onto PANi as seen in IR spectra. From a measurement of humidity sensing behaviour can be seen that PANi/cellulose composite can be used as humidity sensor material.
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