Syntesis Conductive Polymer from Polypyrrole (PPy) Based Assisted by Polyvinyl Alcohol (PVA) Through Batch Polymerization Technique

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Abstract. Polypyrrole (PPy) is one of conductive polymer material has been synthesized through polymerization process using chemical oxidative reaction by batch polymerization technique. The synthesis was conducted at room temperature with agitation speed within 300-500 rpm. The certain amount of pyrrole monomer was reacted with ammonium persulphate in the aqueous media. De-mineralized water is the only one solvent was involved in the reaction. The presence of 0%, 1% and 2% of Polyvinyl alcohol (PVA) in the synthesis of PPy was investigated. Washing process found maximal after four times washing indicated by FTIR spectrum, physical appearance, color and conductivity value of the filtrate of residual washing treatment. While the synthesized PPy with presence of PVA obtained higher conductivity compare when PVA free. The conductivity value was 57,000, 56,000 µs/cm for additional 1% and 2% of PVA respectively. It is significantly increased when PVA free involved in the reaction. Other supporting characterization during synthesis was conducted such as pH measurement, density, viscosity, temperature and colour degradation observation. The appearance of PPy when presence PVA is being emulsion and different when absence of PVA which obtained powder or solid form of PPy. Black polymer emulsion with various viscosity of PPy was observed completely.

1. Introduction
In the past 45 years, research on conductive polymers continues, from the discovery of polyacetylene as the first conductive polymer discovered by Hideki Shirakawa, Alan Heeger, and Alan MacDiarmid [1], until now research on conductive polymers still needs to be done. Conductive polymers are polymers that have conjugated electrons along the polymer chain and contain delocalized electron structures. When compared to the usual types of polymers, the uniqueness of polymers charged with macro-charged polymers, from oxidative polymerization, as well as morphology that can conduct electricity and seek rapid response as sensors [2,3]. There are 3 types of conductive polymers known today such as the aromatic cycle with polyaniline [4], polypyrrole [5], and poly (3,4-ethylenedioxythiophene) [6] therein, double bonds using polyacetylene [1] can also be found as follows intermediate is polyphenylene vinylene [7]. Extensive application of polymers, including to replace functions that cannot be carried out by metal. Antistatic coatings, protective materials against...
emagnetic interference (EMI), materials for rechargeable batteries, super capacitors and capacitors, and various electrochemical sensors etc., and semiconductor polymers can be used for applications that use more light emitting diodes (LEDs), Fields Effect Transistor (FET), and Photovoltaic (PV) solar panels [8].

In the previous research it has been known that PPy is a promising conductive polymer for the industrial world because of its good stability, flexibility in synthesis and higher conductivity compared to other conductive polymers [5]. According to the previous research PPy can be prepared by dissolving with water and added with anionic surfactant [9]. PPy can be synthesized by various methods including electrochemical and oxidative chemical polymerization where different methods will affect the results obtained. For example, a combination of Fe$_2$(SO$_4$)$_3$ as an oxidant and sodium alkyl sulfonate (NaAS) as an anionic surfactant can increase the conductivity and yield of PPy to 40.7 S/cm and 2.24 g [5]. In recent studies, PPy can be used as a coating of the surface of FeOCl micro particle which results in a significant increase in electrical contact, charge transfer, chloride ion transfer and structural stability of the cathode. Therefore, the stability of the cathode cycle increased from 13.2% (FeOCl) to 82.9% (FeOCl/PPy) retention capacity after 30 cycles.

Polyvinyl alcohol is a dissolved crystalline structure polymer made from polyvinyl acetate through the hydrolysis process. PVA has the properties of adhesiveness, toughness, swelling behavior and lack of toxicity so that PVA can be used in various fields such as textiles, packaging, and biomedicine [10,11]. Research on Polypyrrole and Polyvinyl Alcohol has been carried out such as the synthesis of PPy-PVA composite doped with organic acids such as CSA, DBSA, and p-TSA at room temperature using the oxidation chemical method of polymerization method with the results found by PPy-PVA doped with organic acids more thermally and thermally stable [12].

Based on the results of existing research, the use of PVA in this study aims to increase the conductivity of Polypyrrole and take the mechanical properties of Polyvinyl Alcohol to be combined with Polypyrrole [13].

2. Experimental Method
At room temperature, two kind of solutions were prepared for preparing the basic reference solution PPy without PVA. First step by weighting 5 gram of Ammonium persulfate (APS) solution was dissolved with 100 mL demineralized water (DW) in a mechanical stirrer at 500 rpm until it is dissolved evenly. The second solution was 5 mL of Pyrrole monomer mixed with 100 mL of water in a mechanical stirrer at 500 rpm until evenly distributed. Then the two solutions were immediately mixed in the polymerization flask to go through the process of batch polymerization method and stirred for 4 hours of reaction time. After the polymerization is complete, then the PPy can be filtered and dried immediately by vacuum drying to powder form.

For PPy synthesis with the addition of varying PVA, the three solutions were made. The PVA used is partial hydrolysis PVA which has medium viscosity and also medium molecular weight. With the total base of the solution to be produced is 200 mL, the solution consists of 3.75 g APS dissolved with 75 ml DW, 3.75 mL Pyrrole monomer mixed 75 mL DW, and 2 g PVA is dissolved with 50 mL DW (for 1% PVA concentration). In the container which has been presence of PVA solution, APS and Pyrrole solution is also added for the batch polymerization process by stirring for 4 hours of reaction time.

The synthesized PPy was characterized to identify the properties such as color by Visible Spectrophotometer, pH value by pH meter, conductivity by conductometer, FTIR spectrophotometer and other supporting testing of PPy characterization.

3. Result and Discussion
In the first stage of these research, the observation of washing stage was conducted. The washing process as one of the stage is needed to obtain pure PPy in order to increase purity of PPy. Table 1 shows a series of observations on color degradation of filtrate during washing process. First filtration by 100 ml of DW still has string color of PPy, It shows that there are still many PPy inside of the
residual of filtrate which requires a further washing process. Along with the washing process, the color intensity of the solution decreased. When comparing with the intensity of water as a single solvent the third of filtration almost to zero of Gardner unit.

Table 1. Color Evaluation of Residual on Filtration During Washing Process

| Sample Code | Color (Gardner) |
|-------------|-----------------|
| Filtration - 1 | Not detected |
| Filtration - 2 | 7.9 |
| Filtration - 3 | 3.1 |
| Filtration - 4 | 0.4 |
| Water (solvent) | 0.0 |

In addition, the observation was carried out by pH solution measurement by using pH meter series Metrohm 827 with double digit precision. Figure 1 illustrated the pH of the filtrate solution used getting closer to the pH value of water as the washing frequency increased. Demineralized water was used has pH ~ 7.3 while the pyrrole monomer has pH ~ 4.2. pH solution of filtrate is able to indicate the purity of PPy was formed. When the synthesized PPy still containing small amount of residual monomer of pyrrole, the pH solution tend to more acidic approximately below ~ 6.

![Figure 1. pH Observation of Residual on Filtration During Washing Process](image)

Another supporting parameter that can play a role in determining the purity of PPy formed is by measuring the conductivity value of the filtrate solution. In Table 2 described the conductivity value of each stage of the washing process. Same as explained through observations on the parameters color intensity and pH value of filtrate solution, conductivity value can also determine the purity of the formed PPy. Conductivity of demineralized water (DW) was determined by Conductometer and obtained 88 μS/cm of conductivity. While the filtered solution that was sampled showed a high conductivity value at the first time of washing process and the conductivity value was decreased with increasing the washing process, where after reaching the fourth of repetition washing process obtained the lowest conductivity. It indicated the formed PPy has higher purity.
Table 2. Conductivity of Residual on Filtration During Washing Process

| Sample Code   | Conductivity (µs/cm) |
|---------------|----------------------|
| Filtration - 1| 48600                |
| Filtration - 2| 7000                 |
| Filtration - 3| 600                  |
| Filtration - 4| 240                  |
| Water (solvent)| 88                   |

To ensure that the washing process is maximized, spectra FTIR measurements are taken by using FTIR Spectrophotometer type Thermo Nicolet iS5. Through Figure 2 explains the wavenumber mentioned in the range of 1700 - 1500 cm⁻¹ indicating of C=C bonds in the molecule was read at 1630 cm⁻¹, 860 - 660 cm⁻¹ bonding of C-H in the molecule indicated at 660 cm⁻¹ and 3500 - 3300 cm⁻¹ is belong to N-H bonding in the molecule. The three of mentioned spectra is specific indicating the spectra of Pyrrole monomer or it’s derivative. The observation made on the washing process to obtain PPy with high purity through evaluation of parameters color intensity, pH value, conductivity and the FTIR spectrum confirmed the previous research that has been done on the synthesis of PPy which has different focus area [14, 15].

Figure 2. FTIR Spectrum of Residual on Filtration During Washing Process

In order to know the effect of PVA content into pH formed PPy, pH measurement during polymerization reaction was conducted for 4 hours of reaction time. Referring to Figure 3 can explain clearly that pH of solution during reaction is not significant different when presence nor absence of PVA. The range of pH solution is ~ 3.5 – 5.6 which is indicating the pH of final formed PPy was produced through this polymerization reaction. The pH of pyrrole monomer ~ 4.2 does not change significantly when the polymer has formed.
Another observation made during the polymerization reaction is the change in the temperature of the solution. Temperature changes that occur in three different types of reactions do not show high differences. In other words that the additional of PVA into polymerization reaction does not give any impact to temperature reaction. The observation of temperature obtained during the reaction shows in the range between 25-35 °C as figure out at Figure 4.

The focus of this research is the conductivity value of the obtained PPy hence the determination of the conductivity value becomes the main parameter that must be conducted during the...
observation. Table 3 has provided an overview of the results of the conductivity values of each test sample that involves the influence of the presence of PVA in the polymerization reaction carried out. The pure of demineralized water has conductivity value is 88 µs/cm, while for single solution of PVA 1%, 2% and 3% are 100, 150 and 210 µs/cm respectively. The single substance for each material with different concentration had low conductivity. It is totally different when PVA involved into polymerization reaction of PPy. PPy was synthesized when absence of PVA produced a material polymer with conductivity value is 35870 µs/cm and it increased almost two times higher when additional of 3% PVA solution added into polymerization reaction. The additional PVA into synthesis of PPy can increase the conductivity value of formed PPy.

Table 3. Conductivity Value of PPy with Various of PVA Content

| Sample Name         | Conductivity (µs/cm) |
|---------------------|----------------------|
| PPy without PVA     | 35870                |
| PVA solution 1%     | 100                  |
| PVA solution 2%     | 150                  |
| PVA solution 3%     | 210                  |
| Ppy with PVA 1%     | 55000                |
| Ppy with PVA 2%     | 57000                |
| Ppy with PVA 3%     | 62870                |

4. Conclusion

According to the result of research conducted, obtained the information that the additional of PVA content can increase the conductivity value of PPy by reaching two times higher from 35870µs/cm when absence of PVA to 55000, 57000 and 62870µs/cm of PVA content 1%, 2% and 3% respectively.

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