Comparative Studies on the Synthesis of Polypyrrole through Polymerization Reaction Between Batch and Continuous Processes

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Abstract. Comparative studies on conductive polymer of Polypyrrole (Ppy) synthesized through oxidative polymerization in batch and continuous techniques is reported. The common step for the preparation of solutions consisted of mixing between monomer and ammonium peroxidosulphate (APS) solutions with volume ratio 1:1 under an agitation speed of 400 rpm for 4 hours of reaction time. The two different techniques of polymerization resulted in powder of Ppy which confirmed by the standard Fourier Transform Infra Red (FTIR) spectrum. Formation of Ppy occurred in a much faster speed in a batch technique in comparison with that of continuous one. The advantage of continuous process in obtaining the pure Ppy is that it requires a simple washing step with distillate water. Ppy that resulted from a synthesis of the two processes has electrical conductivity value, making Ppy a conducting polymer.

Keywords: Conductive polymer, Polypyrrole (PPy), Chemical oxidative polymerization, Polymerization technique

1. Introduction
Polymeric based materials in general being considered as lighter weight and insulating materials. Current development on the use of polymer materials shown that the polymer has met a variety of applications which are not limited only being used as passive materials due to its isolative properties, but also being used as active materials that hold optical, conducting, and electromagnetic properties [1]. In addition, polymer materials have also extended its potential uses in the areas of energy storage devices [2] and possibly in the area of magnetic applications since polymer with magnetic properties has been reported [3]. The study of polymers that related to the electronics and electrical properties is being carried out intensively to date [4]. One of the objectives is exploring its electrical conductivity which can be generated through ordered conjugation with extended π electrons and sufficiently large electric charge concentration. Hence, the presence of conjugated double bonds along the backbone of the polymer is a key property which must be owned by conductive polymers [5].

In the past, the conductive properties of polymer based material were obtained through embedding the highly conductive particles like graphite, gold, silver powders into a polymer matrix [6]. However, the conducting polymers that prepared through this manner have been proven ineffective due to insufficient value of electrical conductivity obtained from the polymer and deteriorations of physical
properties of the polymer itself. In the last two decades, intensive studies have been addressed to generate the electrical conductivity in polyaromatic backbone polymers. Among them, polyaniline (PANI), Polypyrrole (Ppy) and polythiophene (PT) are considered potential candidates for development of conducting polymer type materials [7]. However, large attentions have been given to the Ppy because in addition to its high electrical conductivity value, Ppy is chemically stable with good mechanical properties and can be synthesized through a simple process. Not surprisingly, the conducting Ppy has met applications in various areas like light-weight batteries, electronic devices, sensors and membrane separation [8]. Another potential application areas of Ppy are drug delivery, rechargeable batteries, supercapacitors, microwave shielding and corrosion protection [9].

The preparation of conducting polymer is mostly carried out either through chemical reaction or electrochemical method. The synthesis of polymer by either of these methods depends upon the intended application of the polymer. The chemical route usually involves a polymerization reaction of monomer which carried out in the reactor [10]. It is a simple, fast and the chief synthesis method since no special instruments are required. The polymerization reaction is ended with resulting in a fine powder obtained after oxidative polymerization of the monomer by chemical oxidants in aqueous or non-aqueous solvents taken place during reaction [11]. Hence, large quantities of polypyrrole (Ppy) can be made through such preparation method. Nevertheless, a number of alternative synthesis methods of Ppy had been introduced by the researchers. Among the methods are electrochemical [12], chemical oxidative polymerization [13], a method which involving self-degradation of template [14] and micro emulsion polymerization technique [9]. Subject to the sequence of method development which are available, the chemical oxidative polymerization was found to be the most attractive and favorite method for synthesis of Ppy. This was indicated by the number of research results that reported results of synthesis of the PPy through chemical oxidative polymerization reaction [15]. When the oxidative chemical polymerization method is selected for synthesis of Ppy, an oxidation agent is required. For instance, ferric chloride, ammonium persulfate can be used as an oxidant for synthesis of pyrrole through oxidative chemical polymerization [8]. It was reported that PPy was formed due to a coupling agent reaction between radical cations from oxidant agent and monomer.

In the present paper, we report results of comparative studies on the preparation of polypyrrole through chemical oxidation method between continuous and batch processes. Ammonium Peroxidisulphate was used as the oxidant to be reacted with pyrrole monomers. Results of comparison studies include molecule formation, color degradation during washing and the electrical conductivity of Ppy.

2. Experimental method

Pyrrole (Sigma Aldrich, 99.9%) and Ammonium Peroxidisulphate (Sigma Aldrich, 99.8%) as a monomer and oxidizing agent respectively were used for Ppy preparation. The monomer solution was prepared by mixing 5 ml pyrrole with distilled water and stirred for 10 minutes to form 100 ml monomer solution. The initiator solution was found by mixing 5 grams of APS with distillated water and stirred for 10 minutes to form 100 ml solution.

In a batch process, the polymerization reaction was carried out under mixing between the monomer and initiator solutions with the volume ratio 1:1, and continuously stirred with a constant speed 400 rpm for 4 hours at room temperature. The process has resulted in powder containing solution which was then filtered out under vacuum and subsequently washed using distilled water for several times to remove any impurities present. The resulted powder was then dried in desiccator for 3 days. For a continuous process, the same ratio of monomer and initiator solutions was applied to prepare the solution. However, the mixing of the two solution was carried out under drop by drop mixing during the polymerization reaction at room temperature for 4 hours under the same constant stirring speed. Afterwards in the polymerization process finished, the resulted powder was filtered, washed and dried by the same treatment as batch technique.

The chemical bonding was analyzed using FTIR spectroscopy by FTIR spectrometer model Thermo Scientific Nicolet iS5 system using Diamond ATR during the whole reaction and washing process.
Gardner Color Scale by Lovibond Spectrophotometer was used to see any product or impurities left after washing process. The conductivity was tested by Four-Point Collinear Probe. This technique involves bringing four equally spaced probes in contact with a material of unknown resistance. The electrical conductivity was then calculated from the slope obtained from an ohmic relation between the voltage and electrical current.

3. Results and discussion

3.1. Polypyrrole Characterization

Figure 1 compares the FTIR spectra of powder obtained after 5 and 240 minutes polymerization reaction in a batch process. The two spectra is almost identical but a slight different in values of peak absorbances. The specific finger print of PPy consisted of a molecule group with peaks absorbance at 1197 cm\(^{-1}\), 1103 cm\(^{-1}\) and 1054 cm\(^{-1}\) belongs to respectively C-N stretching, C-H in-plane deformation and N-H in-plane deformation [8,16]. FTIR spectra in Figure 1 show the presence of characteristic absorption bands at 1452 cm\(^{-1}\) (C=C stretching of pyrrole ring), 1196 cm\(^{-1}\) (C-N stretching vibration in the ring), 1102 cm\(^{-1}\) (C-H in-plane deformation), 1052 (N-H in-plane deformation), 887 cm\(^{-1}\) (C-H out-of-plane deformation), 748 cm\(^{-1}\) (C-H out-of-plane ring deformation). Such set of absorption characteristic is match with that of standard Ppy [8,16]. Obviously, the formation of Ppy molecules already occurred within 5 minutes reaction but the yield is still relatively low.

![Figure 1. FTIR spectra of powder obtained in the batch technique after 5 and 240 minutes reaction time.](image)

FTIR spectra of the powder obtained after 5, 15, 30 and 240 minutes polymerization reaction in a continuous process is compared in Figure 2. Once again, the all spectrums are almost identical, but those of shorter reaction time (5 and 15 minutes), an additional absorbance peak present in each spectrum indicating the Ppy molecules were still not formed completely. Only after 30 minutes reaction time such additional absorbance peak disappears from the spectrum. Hence, when compare results of Figure 1 and 2, it can be concluded that the two processing methods have resulted in different mechanism of Ppy formation. In the batch technique, polymerization reaction occurred through the effective reaction which indicated by the no change spectrum profile.

The formation rate of Ppy in the batch process is much faster than that of continuous processes. The Ppy molecules have formed in the batch process at only in the first 5 minutes reaction time. This was...
not the case in the continuous process from which the reaction time for a complete formation of Ppy molecules is required up to 30 minutes.

Figure 2. FTIR spectra of polypyrrole was synthesized through continuous technique.

3.2. Color degradation
Washing process was carried out three times using distillate water. This process is required to find out if any impurities of product still left after filtered with Whatman 42 and washing process. Products that resulted from this step was then evaluated by Gardner Color Scale Spectrophotometer.

Figure 3. Color degradation of filtrates (a) batch technique and (b) continuous technique.

Figure 4. Color Scale Gardner value of batch and continuous techniques.
Figures 3(a) and 3(b) show photos of color degradation of the filtrate after each washing treatment for the Ppy powder obtained from the batch and continuous processes. The color scale for each filtrate of batch process is compared with that of continuous process in Figure 4. Referring to result in Figure 3 and 4, results show that for batch system, the color degradation did not significantly change after three times washing process by water. It is also confirmed by results of FTIR evaluation in Figure 5(a) for washing powder obtained from a batch process. Other chemical molecule probably the monomer in addition to polypyrrole still exists after washing process. Hence, washing ppy of batch process with water seems less effective. Other suitable solvent for the washing process in this batch system is required. On the other hand, the continuous system gives different result as the color degradation
changed significantly and almost nothing left on the filtrate after the whole washing process. It is shown in Figure 3 (b) where at the third washing the filtrate has color similar to that of distillate water. Hence, in term of color degradation in washing treatment the continuous technique gives much better result after three times washing compared with that of the batch. It was confirmed by FTIR spectra in Figure 5(b) that there are almost no absorbance peaks of Ppy can be observed in a FTIR spectrum of filtrate obtained after third washing treatment. It indicates that the filtrate was already free from other chemical molecules.

3.3. Electrical Conductivity

Figure 6 shows ohmic plots between electrical voltage and current of samples made of compacted Ppy obtained from batch and continuous processes. The resistance (R) value of each sample was determined from the slope of respective ohmic lines in Figure 6. The slope value of each samples differs only slightly indicating that the electrical resistivity or conductivity for the two samples has no large different. It was obtained that the calculated value of electrical conductivity for batch technique was 0.160 S/m, whereas for that of continuous was 0.163 S/m. Despite the value of electrical conductivity of the two samples is still low, however, ohmic plots of samples confirmed the sample is conducting polymer. In the previous reports, we explored the electrical conductivity properties of doped polyaniline in which doping the polyaniline with a strong acid of HClO₄ resulted in the conductivity value of 3.6 S/cm [3]. Result of current studies on the Ppy has confirmed that the Ppy is conducting polymer. Hence, the enhancement of conductivity value in Ppy will be the subjects of our future studies.

![Figure 6. Electrical conductivity of Ppy samples obtained from batch and continuous processes](image)

4. Conclusion

Results of current works have confirmed that Polypyrrole (Ppy) can be obtained through the oxidative polymerization reaction in batch and continuous process. The two processes differ only in the rate of Ppy formation where the batch process is much faster than the continuous one. The advantage of the continuous process in comparison with that of batch is that the continuous process requires only a simple washing treatment in which within three steps washing with distillate water, the Ppy has freed from other molecules. PPy obtained from the two processes has property of electrical conductivity.

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