Surface area and conductivity of polyaniline synthesized under UV irradiation

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Abstract. This paper reports our study on the synthesis of high electrical conductivity and surface area polyaniline using oxidative polymerization under UV light irradiation. The formation of emeraldine structures of polyaniline was revealed by major absorption bands of FTIR (Fourier transform infrared spectroscopy) spectra attributed to C-N stretching, C=C stretching in the benzenoid ring, C=C stretching in the quinoid ring and QNH^+B stretching. XRD (X-ray diffractometer) measurements confirmed typical diffraction patterns with a crystallinity of 13% and 16% for polyaniline prepared under non-stirred and stirred reaction, respectively. SEM (Scanning electron microscope) studies showed more uniform morphology of polyaniline was obtained with stirring reaction process compare to those prepared without stirring. Surface analysis using SAA (surface area analyzer) showed that pure polyaniline with the relatively high surface area of ca.28 m^2/g was successfully prepared in this work. Based on four point probe measurement, the prepared polyaniline possesses high conductivity which is important in electrode application.

1. Introduction

A conductive polymer such as polyacetylene, polypyrrole, polythiophene and polyaniline are well-known materials that have been developed for much-advanced application in various devices. Amongst of these polymers, polyaniline in the form of emeraldine salt has attracted a remarkable attention due to its excellent properties, namely high conductivity, good electrochemical properties and redox reversibility, high electrical and environmental stability as well as simply in fabrication process [1, 2]. In addition, the commercial monomer for polyaniline is available in relatively low price. These advantageous characteristics make polyaniline has potential application in numerous devices such as chemicals sensor [1], toxic gas sensor [3], electrode [4], supercapacitor [5], solar cell technology [2] photovoltaics and thermoelectric energy conversion [6].

Polyaniline could be synthesized by means of oxidative polymerization and electrochemical polymerization techniques. Oxidative polymerization is a low cost and simple route for polyaniline preparation without any particular instrument made this approach used in many reported studies [7]. Physical and chemical properties of polyaniline are influenced by synthesis condition, e.g. solution

concentration and composition, reaction temperature, stirring, dopant and pH of the solution system [8]. For instance, radical reaction rate controlling elongation processes in the polymer chain that affect molecular weight of polyaniline is known to rely on the reaction temperature. At which the molecular weight is recognized as one of the factors that determined polyaniline conductivity. Since electrical conductivity and surface area of polyaniline are important for its application, many attempts have been carried out to enhance the values of both properties, mostly by engineered polyaniline with other materials e.g. graphene [5, 9], titanium dioxide [10], and carbon nanotubes. However, based on some previously reported works [9, 11–13], conductivity and surface area of pure polyaniline are still need to be improved.

This study is intended to develop polyaniline with high conductivity and surface area through Ultra Violet (UV) light irradiation at initial reaction temperature of 0°C. UV exposure during polymerization can induce the formation of fine polyaniline structure [14] which may increase its surface area. Consequently, performance of the obtained polyaniline produced can be increased its performance in a suitable application.

2. Method

Polyaniline was synthesized by oxidative polymerization method using 0,2 M aniline solution prepared in 0,2 M HCl and 0,1 M Ammonium Peroxydisulfat (APS). These solutions were cooled down using ice bath until its temperature reach 0°C. Then, the ammonium peroxidisulfate solution was slowly poured into the aniline solution with continuous stirring on the magnetic stirrer. Further polymerization was performed under UV light irradiation using UV laminar air flow for 1 hour applied for both non-stirred and stirred reaction process. The obtained polyaniline powder was then separated from its solution by centrifugation, rinsed by aquadest and dried at room temperature subsequently. This powder was then used to make polyaniline film under vacuum mounting press at room temperature.

FTIR spectra of both powder and film form of the polyaniline were obtained using Fourier Transform Infrared Spectroscopy (Shimadzu IR Prestige-21) at wavenumber ranging from 400-4000 cm^{-1}. Crystallinity degree was examined by X-ray Diffractometer (PANalytical EMYREAN) using Cu Kα radiation with λ=1.54187. Morphological analysis was carried out with Scanning Electron Microscope (JEOL JSM-6510LA). Measurement electrical conductivity of the polyaniline film was performed using four point probe (Keithley 2700 Nanovoltmeter and Keithley 6200 Current Source). Surface area and porosity of the polyaniline were measured by Surface Area Analyzer (Micromeritic ASAP 2020).

3. Results and Discussion

FTIR spectra of the synthesized polyaniline through oxidative polymerization under UV light irradiation both from non-stirred and stirred reaction are presented in Figure 1. The figure indicates absorption characteristics of emeraldine salt form of polyaniline by the existence of the bands of N-H, C-H, C=C (Q), C=C (B), C-N, dan Q=NH$^+$-B that are assigned as follows. An absorption band observed at the wavenumber of 3400 was attributed to N-H stretching. The bands at 2900 cm^{-1} were attributed to stretching of C-H asymmetric and C-H symmetric. The bands at 1500 cm^{-1} and 1467 cm^{-1} for polyaniline obtained from non-stirred polymerization were associated to stretching of C=C quinoid and benzenoid, respectively. These bands were shifted to 1610 cm^{-1} and 1516 cm^{-1} for those obtained under stirring reaction. The bands at 1300 cm^{-1} and 1265 cm^{-1} were due to stretching of C-N. The bands at 1113 cm^{-1} and 1107 cm^{-1} were associated with the presence of Q=NH$^+$B which is the main characteristics of emeraldine salt form of polyaniline. These strong absorption bands related to good electrical conductivity of the obtained polyaniline [15].
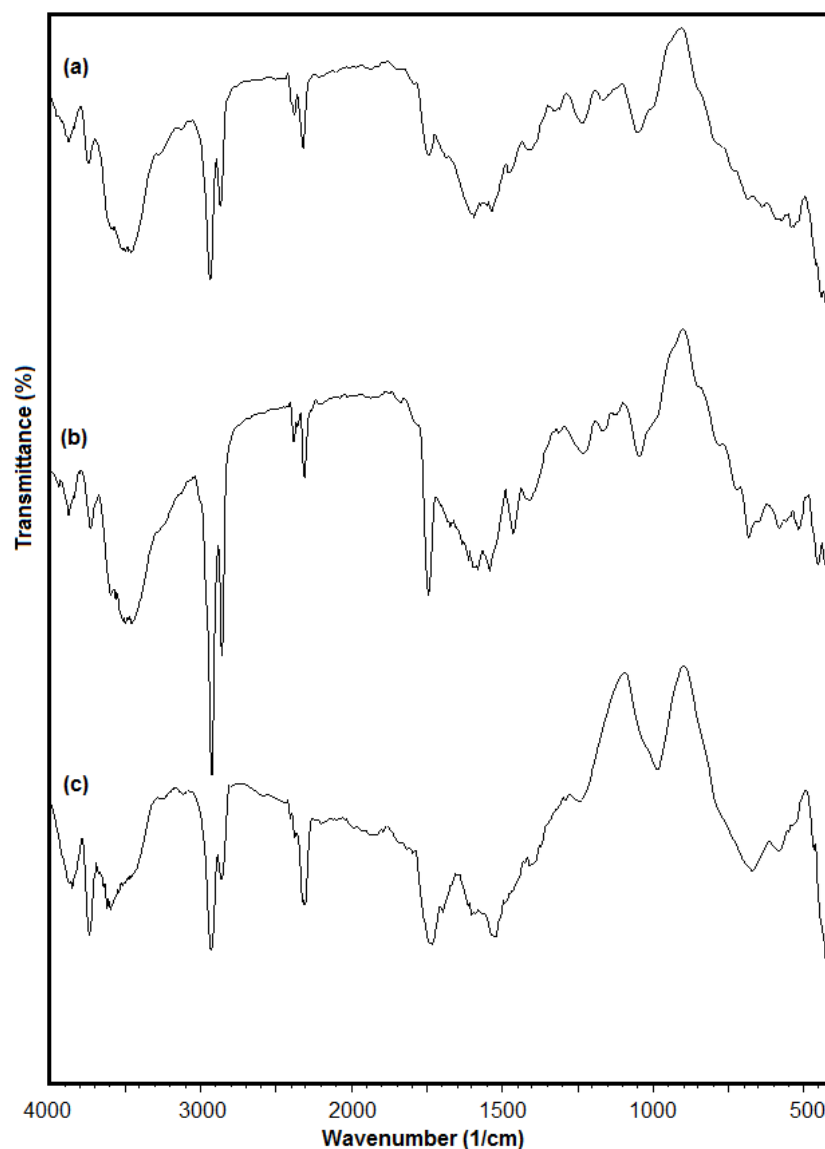
Figure 1. FTIR spectra of powder of polyaniline synthesized without stirring (a), with stirring (b), and film of the polyaniline (c)

Morphological analysis of the polyaniline was carried out using a scanning electron microscope (SEM). The micrograph shown in Figure 2 shows that polyaniline synthesized without stirring formed nanofiber with 100-200 nm diameter. Few granular polyaniline were also observed in the micrograph. In addition, the non-stirred reaction caused the difference of polymerization environment that resulted in not uniform morphology. Due to the direct exposure of UV irradiation, more rapid growth occurred at the surface compared to inner part of the system. Meanwhile, the stirred polymerization showed more uniform morphology with the fine diameter of 70–90 nm due to well distribution of UV light irradiation during polymerization process [5].

Figure 3 shows diffraction patterns of polyaniline obtained from the X-ray diffractometer (XRD) measurements. For polyaniline obtained from non-stirred reaction, the diffraction peaks appeared at 2θ 20.31° and 25.26°. The peaks were found to slightly shift to 2θ 20.55° and 25.59°, respectively, in the XRD pattern of polyaniline prepared under stirred reaction. After treatment with the mounting press, it is observed that there was no significant change in their diffraction patterns, although the first peak slightly shifted to 2θ 19.04° and 19.79° for the samples synthesized under non-stirred and stirred

reaction, respectively. Those are the main peaks indicating the formation of polyaniline, at which the first represents amorphous form and the second one corresponds to a crystalline structure of the polyaniline [16–20]. Benzenoid and quinoid rings in polyaniline chain have the major role to form a crystalline structure in the emeraldin structure of polyaniline [19]. The measurement results carried out using HighScore Plus software showed that crystallinity degree of non-stirred and stirred synthesized polyaniline were 13.21% and 14.56%, respectively.
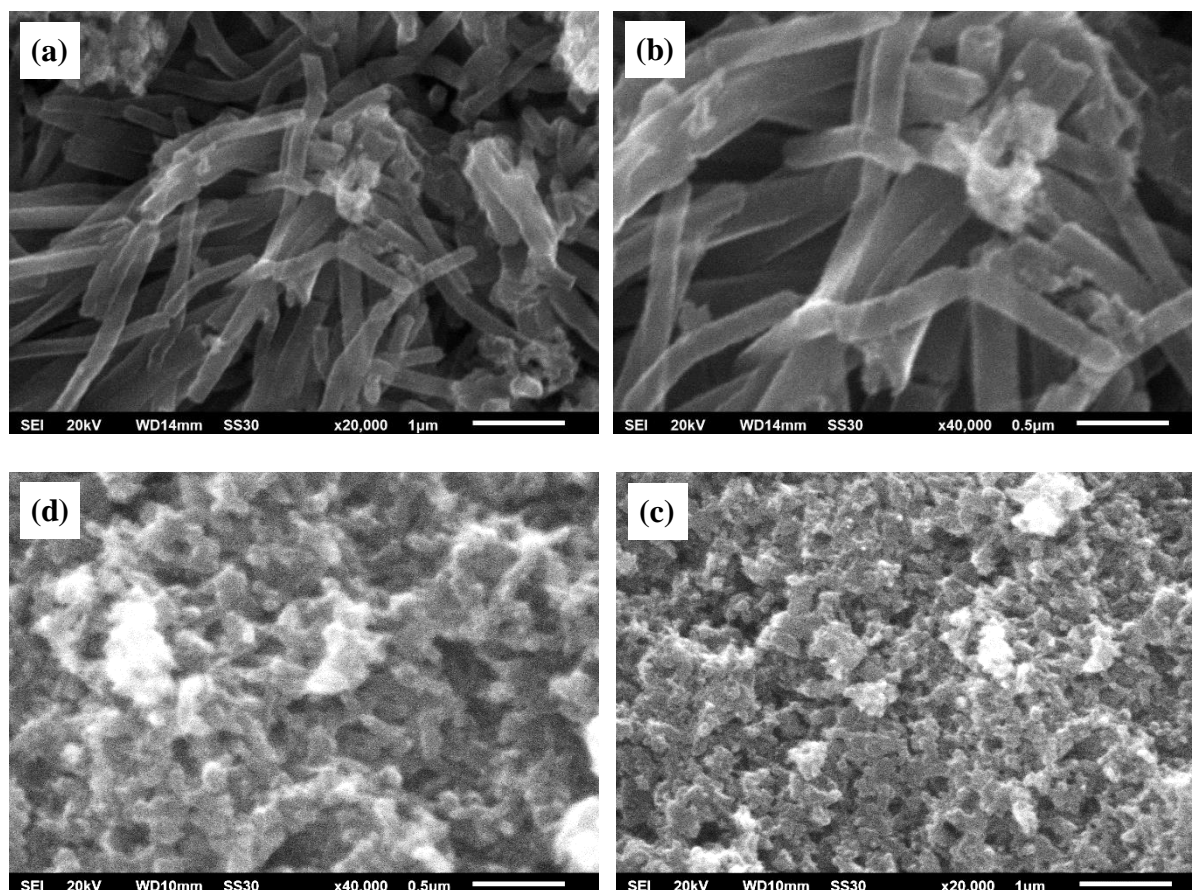

Figure 2. SEM micrograph of polyaniline prepared without (a and b) and with stirring condition (c and d).

Surface area and porosity of the polyaniline were determined using surface area analyzer (SAA) Micromeritics ASAP 2020. Figure 4 shows type IV characteristics of nitrogen gas (N_2) adsorption-desorption of powder polyaniline. Hysteresis loops appeared at relatively high pressures of 0.8 P/P_0 for the polyaniline both prepared under non-stirred and stirred reaction. There was a remarkable rising of the adsorption volume when the condensation took place at high pressure. This hysteresis loop was caused by capillary condensation inside the mesopore [12]. From the curves, both polyanilines show similar hysteresis characteristics indicating typical porous which correspond to mesoporous material type. Distribution of pore size was then measured by Barrett-Joyner-Halenda (BJH) method. The distribution of polyaniline pore size showed average size at 19.8 nm and 17.1 nm respectively for polyaniline prepared under non-stirred and stirred reaction. These sizes were ranging from 2-50 nm and d>50 nm for both mesopore and macropore, respectively. BET surface area of the polyaniline synthesized without stirring was 27.07 m^2/g while with stirring was 28.68 m^2/g. This result shows that

this approach produces high surface area of polyaniline compared to those reported previously i.e., 20.02 m^2/g dan 15.38 m^2/g [9, 12]. This condition may catalyze rapid electron transfer and high ion diffusion which could enhance electrochemistry performance of the polyaniline. In addition, it may also generate direct conduction path for electron [12].
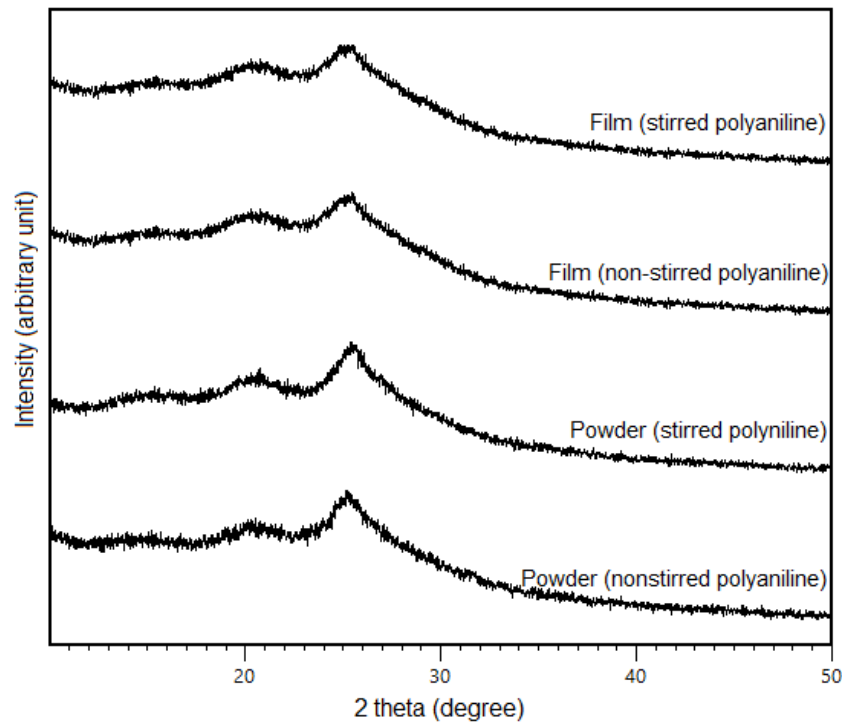

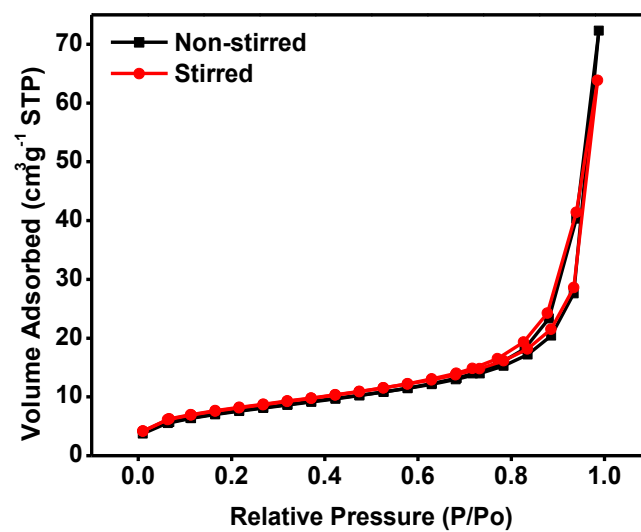**Figure 3**. XRD pattern of synthesized polyaniline

Figure 4. N_2 adsorption/desorption isotherm of the synthesized polyaniline

The conductivity of polyaniline measurement was carried out using four point probe. The obtained data was resistivity value (R). The conductivity was then calculated based on the following equation:

$$R = \frac{V}{l} = \rho \frac{x}{A} \tag{1}$$

$$\sigma = \frac{1}{\rho} \tag{2}$$

which R = resistance (Ω), ρ = resistivity (Ω.m), l = length (cm), A = cross-sectional area (cm^2) dan σ = conductivity (S/cm). The conductivity values of non-stirred and stirred polyaniline were 4.34 x 10^{-1} S/cm and 3.48 S/cm, respectively. The values indicated that polyaniline prepared under stirred reaction has higher conductivity than that of non-stirred. This condition could be related to morphology of the stirred reaction polyaniline which was fine and homogenous with a high surface area as revealed by the SEM and SAA results. These characteristics of polymer structures can improve electron transfer resulted in high conductivity of emeraldine salt of polyaniline. The result shows that electrical conductivity of pure polyaniline obtained from this work is higher than those reported in previous studies [11]. This suggests that UV irradiation can be employed to enhance the conductivity of emeraldine salt of polyaniline significantly.

4. Conclusion

Polyaniline in the conducting form emeraldine salt was prepared by oxidative polymerization under UV light irradiation with an initial polymerization temperature of 0°C. The obtained pure polyaniline shows high electrical conductivity as well as high surface area. It is found that stirring during polymerization process influences the growth characteristic and resulted in fine nanofiber and uniform morphology of the polyaniline. Though stirring do not affect crystallinity degree of polyaniline. The electrical conductivity of the emeraldine salt of polyaniline obtained from stirring reaction is eight times higher than those obtained from non-stirred polymerization. Owing to its high conductivity and surface area, the synthesized pure polyaniline might be a potentials material for electrode application.

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