

Synthesis and Characterization of High Conductivity Polyaniline Prepared at Room Temperature

Devi Indrawati Syafei¹, Eka Puspa Rini², Maria Paristiwati³, Agung Imaduddin⁴, Setia Budi^{2,*}

¹The Centre for Science Innovation, Jl. Utan Kayu Raya, Jakarta 13120, Indonesia

²Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Jakarta, Jakarta 13220, Indonesia

³Department of Chemistry Education, Faculty of Mathematics and Natural Sciences, Universitas Negeri Jakarta, Jakarta 13220, Indonesia

⁴Research Center for Metallurgy and Materials, Badan Riset dan Inovasi Nasional, PUSPIPTK Area Building 470, Banten 15314, Indonesia

*Corresponding author: setiabudi@unj.ac.id

RECEIVED

25 November 2021

ACCEPTED

29 January 2022

PUBLISHED ONLINE

28 February 2022



Original content from this work may be used under the terms of the [Creative Commons Attribution 4.0 International License](https://creativecommons.org/licenses/by/4.0/).

Abstract

In this study, polyaniline was successfully synthesized using an oxidative polymerization method at room temperature. The polymerizations were carried out with and without stirring process under ultraviolet (UV) irradiation. The polyaniline was characterized by FTIR, XRD, SEM, SAA, and Four Point Probe. It is found that UV irradiation and stirring could increase the surface area and conductivity of polyaniline. The surface area obtained for stirred and unstirred polymerization were 37.9 m²/g and 29.0 m²/g, respectively. Moreover, conductivity values for stirred and unstirred polymerization were found as 1.22 S/cm and 1.08 S/cm respectively. This result shows that polyaniline synthesized by stirring treatment obtained uniform morphology, smaller size, greater crystallinity, higher BET surface area, and higher conductivity than that of without stirring.

Keywords: High conductivity, polyaniline, oxidative polymerization

1. Introduction

Conductive polymers are attracting because of their advantages due to good conductivity, good stability, and easy preparation [1]. Among conductive polymers, polyaniline is one of the most intensively studied, because its conductivity can be controlled through doping-de-doping, high stability, and more soluble in organic solvents [2]. Besides that, polyaniline has a low-cost monomer and good redox reversibility. Therefore, polyaniline can be an ideal polymer candidate for many applications [3], such as biosensors [4], corrosion protection [5], storage applications [6], and battery charging [7].

There are several methods that can be used to synthesize polyaniline including electrochemistry [8], electrospinning [9], interfacial polymerization [10], inverse emulsion polymerization [11], and plasma polymerization [12]. However, these methods require high energy consumption, high cost, and complicated method due to sophisticated instruments usage. Nevertheless, there is a

method that offers simple and lower costs, namely oxidative polymerization [13].

The physical and chemical properties of polyaniline can be affected by several variables, such as the concentration of aniline, acid and oxidizing agent, a ratio between monomer and oxidizing agent, temperature, and polymerization time [14]. The role of UV irradiation in the synthesis was also known can increase the formation of polyaniline with higher porosity and surface area [15]. It is also known that the conductivity of polyaniline increases with increasing temperature. On the other hand, the conductivity will decrease as the temperature decreases

Based on these facts, this research is intended to synthesize polyaniline by using oxidative polymerization technique and UV irradiation in room temperature will be applied for obtaining high conductivity and surface area of deposit.

2. Materials and Method

The chemical materials used for the synthesis were Merck aniline (PA) 99.9% ($C_6H_5NH_2$) 0.2 M as monomer, Merck HCl (PA) 2 M as an acid dopant, and ammonium peroxydisulfate (APS) (PA) 0.1 M as an oxidant. A total of 1.82 mL of 0.2 M aniline, 1.66 mL of 2 M HCl, and 2.1899 grams of 0.1 M ammonium peroxydisulfate (APS) were mixed at room temperature. The synthesis was carried out with a ratio aniline mole: APS = 2:1. Before the polymerization process, 1.82 mL of aniline and 2.1899 grams of ammonia peroxydisulfate (APS) were added to each of 5 mL of 0.2 M HCl. Then polyaniline was synthesized by mixing the two solutions and then the polymerization process was carried out under UV irradiation using laminar water for 1 hour. In this stage, two stirring variations were applied which were stirred and unstirred solution. The stirred solution was stirred until formation of green precipitate. Meanwhile, the unstirred solution remains untreated until formation of green precipitate as well. The green precipitate was then rinsed 3 times using distilled water. Afterwards, the precipitate and filtrate were separated using a centrifuge. The resulting precipitate was then dried in a desiccator for 3 days. Furthermore, the polyaniline precipitate was made in the form of a film by pressing it with a pressure of 8 tons for 3 hours at room temperature and 3 minutes at 225 °C.

The electrical conductivity of polyaniline films were measured using Keithley 2700 nano voltmeter and Keithley 6200 Four Point Probe. Infra-red spectra were obtained using a SHIMADZU Prestige-21 FTIR Spectrometer. Sample morphology was characterized using SEM JSM-6510LA SEM JEOL. Diffraction patterns of the polyaniline were obtained using PANalytical Empyrean X-ray diffractometer. Surface area was determined using adsorption-desorption isotherm with nitrogen. Samples were measured by degassing at 150 °C for 6 hours carried out by the Micromeritics ASAP 2020 Surface Area Analyzer.

3. Results and Discussion

3.1 FTIR Characterization

FTIR spectra of the synthesized polyaniline are shown in Figure 1. Figure 1a shows typical polyaniline peaks from the sample that synthesized without stirring method. The peaks at wavenumbers 1581.63 cm^{-1} and 1442.75 cm^{-1} represent the presence of C=C stretching of the quinoid (Q) and benzenoid (B) rings, respectively [16]. The peak at wavenumber 2926.01 cm^{-1} indicated C-H stretching on CH_2 [17]. Moreover, the peak at wavenumber 3431.36 cm^{-1} give sign to the presence of N-H stretching of the secondary amine [18]. Some of the bonds in the range of

$2800\text{ to }4000\text{ cm}^{-1}$ were caused by N-H stretching vibrations in the polymer structure and C-H stretching of CH_3 or CH_2 [17]. The typical peak of PANI-ES was observed at 1043.49 cm^{-1} . This peak shows the conductivity band in PANI-ES, namely the vibration of $B-NH^+=Q/B-NH^+$ which formed due to the doping reaction. This peak is very intense and wide. Strong absorption at the peak $B-NH^+=Q/B-NH^+$ were associated with the electrical conductivity and electron delocalization in PANI-ES [19].

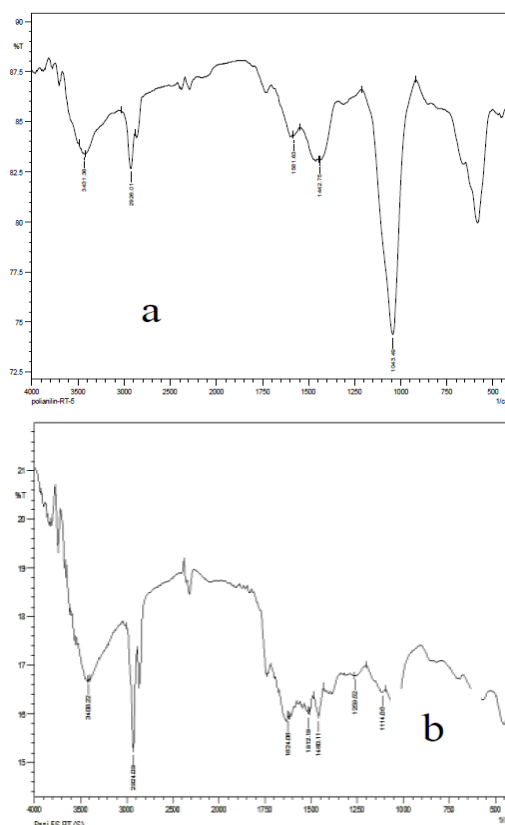


Figure 1. FTIR spectra of unstirred (a) and stirred (b) synthesized polyaniline.

Figure 1b shows the spectra produced by PANI-ES with stirring method. It is known that the peaks at 1512.19 cm^{-1} and 1460.11 cm^{-1} show the deformation of the quinoid and benzenoid rings, respectively. C-N stretching of secondary aromatic amines is shown at 1259.52 cm^{-1} (Vivekanandan et al., 2013). Furthermore, typical peak of PANI-ES is exhibited at 1114.86 cm^{-1} which shows the conductivity band in PANI-ES, namely the vibration of $B-NH^+=Q/B-NH^+$ formed due to the doping reaction as well as unstirred method. This peak is very intense and wide. Strong absorption at the peak $B-NH^+=Q/B-NH^+$ is associated with electrical conductivity and electron delocalization in PANI-ES [19].

3.2 SEM Characterization

Figure 2 illustrates micrograph of unstirred and stirred synthesized polyaniline. Based on Figure 2a, the morphology of the unstirred polyaniline has a non-uniform shape that consists of fiber and granular forms. The fiber diameters were around 100-400 nm. Meanwhile, polyaniline synthesized with stirring treatment has a uniform shape of fibre with diameter about 80-100 nm, as shown in Figure 2b. SEM micrographs of polyaniline samples with stirring method showed better nanofiber characteristics than without stirring. Based on these results, it can be concluded that the sample with stirring method has smaller diameter and more homogeneous than polyaniline which is synthesized without stirring. This is due to the exposure of UV light that can spread to entire surface resulted in enhancing the formation of PANI-ES. In the PANI-ES synthesis without stirring, only the top surface of the solution that was exposed to UV light, consequently the polymerization process did not take place optimally and led to uneven morphology formation [20].

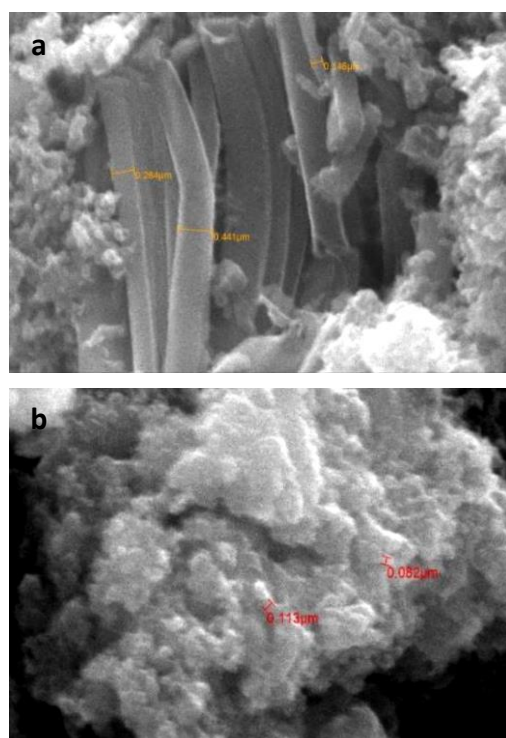


Figure 2. Micrograph of unstirred (a) and stirred (b) synthesized polyaniline.

Based on the SEM results, the morphology of polyaniline synthesized with stirring had a better nanofiber shape than polyaniline without stirring. Hence, the overall diameter of the particles also has a smaller size. This micrograph also shows that the synthesized polyaniline has several pores or cavities. The small polyaniline pores provide a wider surface area which allows it to react more quickly with other compounds.

3.3 XRD Characterization

The diffractogram in Figure 3a shows the XRD diffraction pattern of the PANI-ES film. Based on the results it shows that the amorphous phase and the peak of polyaniline were found at $2\theta = 19.7787^\circ$ and 24.8643° for unstirred PANI-ES RT film and at 8.7823° , 20.7468° , and 25.244° for stirred PANI-ES RT films. The typical peak of polyaniline is at $2\theta = \sim 25^\circ$ [3]. Peak $2\theta = \sim 19^\circ$ indicates amorphous peak of polyaniline and peak at $2\theta = \sim 9.0^\circ$ indicates crystalline peak [16]. This diffraction pattern is almost the same as the diffraction pattern of powdered polyaniline in the PANI-ES film without stirring. Peaks of 9.0° did not appear due to low crystallinity. The crystallinity values obtained for unstirred and stirred polyaniline films were 10.15% and 10.19% respectively.

Figure 3b shows the XRD diffraction pattern of PANI-ES powder. The XRD pattern of unstirred polyaniline-ES powder showed 2 high diffraction peaks at $2\theta = 20.0896^\circ$ and 25.244° . While stirred polyaniline shows peak at $2\theta = 8.7145^\circ$; 20.0067° and 25.612° . The crystallinity values achieved from unstirred and stirred polyanilines were 13.06% and 13.56%, respectively. The amorphous phase and typical peaks of polyaniline were revealed at 19.77° and 24.86° for unstirred polyaniline and at 20.74° and 25.24° for stirred polyaniline. In this characterization, the obtained crystallinity values obtained for unstirred and stirred polyaniline films were 11.21% and 11.09%, respectively.

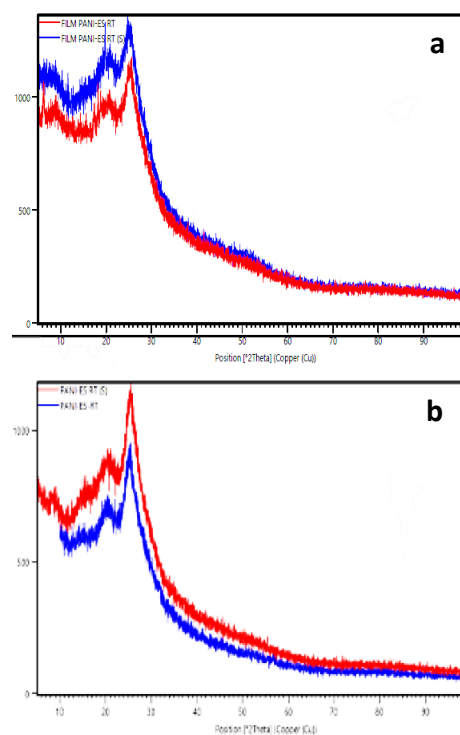


Figure 3. XRD pattern of unstirred (a) and stirred (b) synthesized polyaniline.

3.4 SAA Characterization

SAA works based on the BET (Brunauer Emmett-Teller) method. The BET surface area value produced on polyaniline synthesized without stirring was 29.0072 m²/g and with stirring was 37.895 m²/g. There was an increase surface area of the sample synthesized with stirring in the polymerization process. This result is greater than the value obtained by Ayad et al. (2012) with the same method but without UV irradiation, which was 20.02 m²/g [21]. The increasing surface area can be caused by the influence of the UV irradiation during the polymerization process. It is known that UV irradiation can make polyaniline to become nanostructures with various reaction conditions and maximize the formation of polyaniline nanofibers where these fibres indicate a porous mash-like sample [15]. The large surface area of polyaniline can support fast electron transport and high ion diffusion, thereby improving its electrochemical performance. Polyaniline with large surface area and good electrical performance is a promising candidate in renewable material development applications. Polyaniline with these characteristics can be applied as sensors, energy storage, solar cells, electrodes, and so on. With a large surface area, the application of polyaniline in the material will be more effective.

Figure 4 shows the adsorption-desorption of the PANI-ES without (Figure 4a) and with stirring (Figure 4b) method. It can be observed that the data shows a type IV isotherm with a hysteresis loop around a high relative pressure. For relative pressure values higher than 0.8 during the process, an increase sharp in the adsorption volume was seen. Hysteresis loops occurred due to capillary condensation in the mesopores [21]. This indicates that this sample has a mesoporous type.

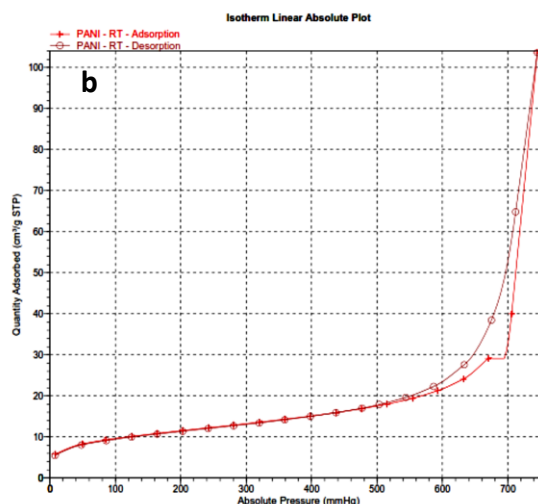
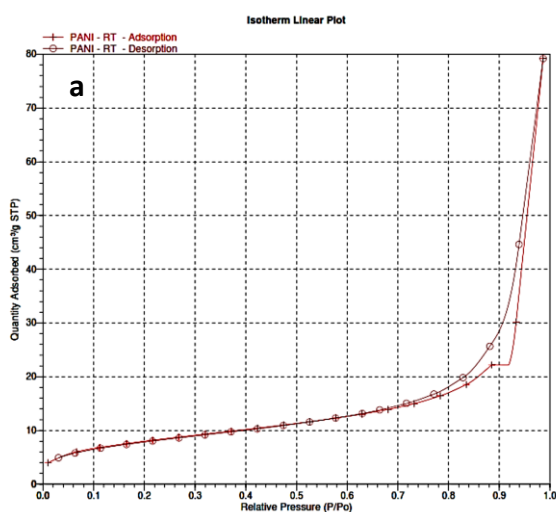


Figure 4. Adsorption-desorption PANI-ES without (a) and with (b) stirring method.

2.5 FPP Characterization

The conductivity value of stirred and unstirred polyaniline synthesized were 1.22 S/cm and 1.07 S/cm respectively. This result is greater than the conductivity value of pure polyaniline that synthesized without UV irradiation process as measured by Vivekanandan et al. (2011), with a value of 0.27 S/cm. The increase in the conductivity value was affected by UV irradiation and stirring process. UV irradiation can increase the formation of a more uniform morphology of the nanofiber structure [22]. Moreover, the stirring process can make the growth of polyaniline more homogeneous, smaller in diameter, and larger surface area. The PANI-ES structure with these characteristics can increase the electron transfer process in the polymer chain and thus increase the conductivity of polyaniline.

4. Conclusion

Based on the results, it can be concluded that a high conductivity polyaniline can be successfully synthesized through oxidative polymerization method under UV irradiation at room temperature. Stirring during polymerization produced polyaniline with a more uniform morphology of fibre, smaller fibre size, greater crystallinity, higher BET surface area, and higher conductivity compare to that of prepared without stirring.

Acknowledgement

This work was supported by research grant (No. 2/E4.1/DSD/LPPM/2021) from Kementerian Pendidikan, Kebudayaan, Riset, dan Teknologi Republik Indonesia.

References

- [1] Molapo, Kerileng M., M.Peter., Ajayi, Rachel F., Mbambisa, Gieneka., Mailu, Stephen M. 2012. Electronics of Conjugated Polymers (I) :Polyaniline. International Journal of Electrochemical Science. Vol 7. Hal 11859-11875.
- [2] Wallace,Gordon G., Spinks,Geoffrey,M., Kane-Maguire, Leon A.P., Teasdale, Peter R. 2003. Conductive Electroactive Polymers. Intelligent Material System. London:CRC Press LLC.
- [3] Bandgar,D.K, Khuspe,G.D, Pauer,R.C. 2014. Facile and Novel Route for Preparation Of Nanostructure Polyaniline (PANI) thin Film. Appl NanosciVol. 4. Hal 27-3.
- [4] Amborsi, Adriano, Morrin, Aoife, Smyth, Malcolm R, Kilard, Anthony J. 2007. The Application of conducting polymer nanoparticle electrodes to the sensing of ascorbic acid. Analytica Chimica Acta. Vol. 609. Hal 37-43.
- [5] Wang, Y,Y,Jing, Xinli. 2004. Preparation of an Epoxy/Polyaniline Compsite Coating and Its Passivation Effect on Cold Rolled Steel. Polymer Journal. Vol 36. No. 5. Hal 374-379.
- [6] Perveen, Nazish, Ansari, Mohd Omaish, Cho Moo Hwan.2015.Route to high Surface Area, mesporosity of polyaniline-Titanium Dioxide Nanocomposite via One Pot Synthesis for Energy Storage Applications. Industrial and Engineering Chemistry Research. Hal 712-749.
- [7] Ghanbari, Khadijeh, Mousavi, Mir Fazlollah, Shamsipur, Mojtaba, Karami, 72 Hasan.2007.Synthesis of Polyaniline/graphite Composite as a Cathode of Zn-Polyaniline Rechargeable Battery. Journal of Power Sources. Vol 170. Hal 512-519.
- [8] Hong-zhi, Wang, Peng,Zhang, Wei-Guo,Zang, Su-wei,Yao. 2012. Electrodeposition and Characterization of Polyaniline Film.Vol 28. No 1. Hal 133-136.
- [9] Zhao,Yunyan, Zhang,Zhiming, Yu,Liangmin, Tang,Qunwei. 2016. Electrospinning of Polyaniline microfibers for Anticorrosion Coatings: An Avenue of Enhancing Anticorrosion Behaviors. Synthetic Metals. Vol 212.Hal 84-90.
- [10] Shedd,B, Baker,C.O, Heller,M.J, Kaner,R.B, Hahn,H.T. 2009. Fabrication of Monolithic Microstructures From Polyaniline Nanofibers. Materials Science and Engineering B. Vol 162. Hal 111-115.
- [11] Rao,Palle Swapna, Sathayarayana, S, Palanniappan,S. 2002. Macromolecules. Vol.35. Hal 4988-49986.
- [12] Cruz,G, J,Morales, J,Castillo-Ortega, M.M, Olayo,R. 1997. Synthetic Metals. Vol.88. Hal 213-218.
- [13] Chairunnisyah, Masayu Farina. 2011. Polimerisasi Interfasial Polianilin dan Aplikasinya Sebagai Indikator Boraks. Depok: Unversitas Indonesia.
- [14] Asri, Novena Damar. 2008. Sintesis dan Karakterisasi Film Polianilin Penggunaan Dopan Asam Sitrat dan Asam Tartrat. Depok: Universitas Indonesia.
- [15] Li, Jing., Tang,Heqing., Zang,Aiqing.,Shen,Xiantao., Zhu,Lihua.2007. A New Strategy for the synthesis of Polyaniline nanostructures:From Nanofibers to Nanowires.
- [16] Ferrokhzad, Hasan., Gerven,Tom Van., Bruggen Bart Van der. 2013. Preparation and Characterization of a conductive polyaniline/polysulfone film and evaluation of the effect of co-solvent. EUROPEAN Polymer Journal. 49.3234-3243.
- [17] Du, Xianfeng., Xu, Youlong., Xiong, Lilong., Bai,Yang., Jianbo, Zhu., Shengchun. 2014. Polyaniline with High Crystallinity Degree:Synthesis,Structure,and Electrochemical Properties.
- [18] Zeng, Xing-Rong., Ko, Tze-Man. 1997. Structure and Properties of Chemically Reduced Polyanilines. Polymers. 39(5).1187-1195.
- [19] Sanches, Edgar,A., Silva, M.S,Jessica da., O, Joelma M de., C, Ferriera Juliana., L, Soares,AmandaL., Santos, Dos., Trovati, Graziella., Fernandes, Edson G.R. 2014. Structural and Morphological Characteristion of Nanostructural Polyaniline Emeraldin-base form (EBPANI). Jurnal of Molecular Structure.
- [20] Olad, Ali., Ilghami, Fahimeh., Nosrati, Rahimeh. 2012. Surfactant-assisted 74 synthesis of polyaniline nanofibers without shaking and stirring effect of condition on morphology and conductivity. Chemical Plymers. 66(8). Hal 757-764.
- [21] Ayad, Mohamad., Zaghlol, Sawsan. 2012. Nanostructured crosslinked polyaniline with high surface area: Synthesis, Characterization and adsorption for organic dye. Chemical Engineering Journal. 79-86.
- [22] Vivekanandan,J., Ponnusamy,V., Mahudeswaran,A., Vijayanand,P.S. 2013. Synthesis, characterization and conductivity study of polyaniline prepared by chemical oxidative and electrochemical methods. Sholars research library.3(6).147-153.