

Homogenization Effect on Nanostructure and Conductivity of Polyaniline Nanofibre Synthesis by Mini-Emulsion Polymerization Technique

M Mohammad¹, S Kamarudin¹, N H Mohamed², N Asim¹, K Sopian¹

¹Solar Energy Research Institute (SERI), Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia

²Malaysia Nuclear Agency (Nuclear Malaysia), 43600, Kajang, Bangi, Selangor, Malaysia

masita@ukm.edu.my

Abstract. Nanofibre polyaniline (n-PANI) was synthesized by mini-emulsion polymerization technique between aniline monomer and ammonium persulfate as an oxidant using homogenizer. The synthesis was performed by optimizing mixing speed from 10,000 to 30,000 rpm and time reaction between 0.5 to 24 hours at fixed monomer to oxidant molar ratio 4:1. An attempt has been made to investigate on how the speed of homogenizer affects the size and conductivity of n-PANI. The formation of n-PANI chain was confirmed by Fourier transform infrared spectroscopy (FTIR). The X-ray diffraction (XRD) spectra revealed PANI crystalline nature. Hall effect measurement used indicated that the electrical conductivity of n-PANI is increased with homogenizer speed from 5.2 to 17.5 Scm⁻¹. The morphological properties of n-PANI performed by scanning electron microscopy (SEM) show the decreasing size of n-PANI from 50-60 nm to 20-30 nm with the increment homogenizer speed. This study indicated the optimum speed parameter of homogenizer play a role in reducing the nanostructured size and thus, increasing the electrical conductivity of n-PANI.

1. Introduction

Polyaniline is one of the most intensively studied conducting polymers with a wide potential application as a functional polymer [1, 2]. Nanofibre polyaniline (n-PANI) is one of the promising conducting polymers due to its environmental stability, controllable electrical properties and high surface area [1]. Electrochemical and chemical methods are the common techniques to synthesized polyaniline and its derivative. Recently, the interests in nano structured PANI have increased tremendously. The mini-emulsion polymerization is known to be a prevailing technique to produce a whole variety of conducting polymer. As compared to the conventional method such as electroplating, mini-emulsion polymerization technique capable of controlling over reaction rates and heat dissipation by applying high shear stress using ultrasonication or high-pressure homogenizer technique [3, 4, 5]. Crystallinity is an indication of the amount of crystalline region in the polymer. High crystallinity will result in high conductivity. The polymer obtains by mini-emulsion method is high crystallinity compare to conventional method [3]. Polyaniline exists in various oxidation states such as pernigraniline, leucoemeraldine and emeraldine. Leucoemeraldine which is fully reduced is environmentally unstable and very reactive even with small amount of oxygen. While pernigraniline is fully oxidized which caused fully imine group and tend to not oxidized, hence environmental friendly.



Emeraldine which is partially oxidized is chemically and environmentally stable. However, the only emeraldine is conducting while pernigraniline and leucoemeraldine are both an insulator. [6].

This surfactant-free emulsion polymerization method is a facile technique to prepare the PANI nanofibers for higher yield and conductivity without application of surfactant. This technique also provides uniform and well-distributed n-PANI without contaminating of surfactants. The surfactant is a substance that lower the surface tension between two liquid. Surfactants such as dodecyl benzene sulfonate (DBSA) and Sodium Dodecyl Sulphate (SDS) are the common surfactant in the polymerization of polyaniline [7]. However, the post-process of removing the surfactant will be an issue in order to get high purity of PANI.

This research aims to study the electrical conductivity and size of n-PANI nanofibers at different homogenizing speed and time reaction. The FESEM, XRD and FTIR techniques were used to analyse the properties of n-PANI.

2. Materials

Aniline (R&M), Chloroform (R&M), nitric acid 70% (QREC), Ammonium persulfate (R&M) and Acetone (QREC). All chemicals are in analytical grade.

3. Methodology

The n-PANI was prepared by mini-emulsion polymerization technique. Typically, in 500 ml conical flask, 9.3g aniline was dissolved in 200 ml chloroform (CHCl₃, analytical grade). The flask was covered with parafilm. In another beaker, 5.7g of ammonium persulfate (APS) was dissolved in 200 ml, 1M nitric acid and the beaker was covered with parafilm to avoid evaporation. A mixture of aniline with chloroform and APS with nitric acid were stirred moderately with a magnetic bar for 30 minutes in a separate beaker. After 30 minutes, APS was transferred into aniline solution. These two solutions were mixed rapidly in exactly 3 minutes by homogenizer with the different speed which was 10 000, 20 000 and 30 000 rpm respectively to study the effect of homogenizer speed in nanofiber formation. Mixing with magnetic stir was done as a reference. After homogenized, the flask was covered with parafilm with no stirring to get the interfacial polymerization effect and kept at room temperature in a comparison time which was 0.5, 1, 2, 4, 6, 15 and 24 hours. After specific hours, 100 ml acetone was added to the flask to stop the polymerization. The product was filtered and washed carefully with 0.1M nitric acid and followed with acetone until the filtrate becomes colourless and finally dried in oven 40 °C for 24 hours [8-10].

The n-PANI will be characterized by Fourier transform infra-red (FTIR) Spectroscopy, (Spectrum 2000 Explorer; Perkin Elmer Cetus Instruments, Norwalk, CT) to confirmed and analyse the functional groups present in the n-PANI. The n-PANI pellet for x-ray diffraction measurements was prepared by using manual hydraulic pressure using 15-tonne pressure. Powder X-ray diffraction pattern was recorded by DS Advanced, Bruker. TGA Thermal gravimetric analysis of the n-PANI prepared under the optimal condition was carried out using thermogravimetry analyser Perkin Elmer Pyris1 to study n-PANI thermal stability. About 4 mg of n-PANI was weighed into an alumina crucible and the thermogram was recorded from 25 °C to 800 °C at a heating rate 10 °C/min under 20 mL/min N₂ flow. The morphology of the n-PANI was examined by FESEM (GEMINI, ZEISS). Room temperature electrical conductivity measurements were carried out by and hall effect study on compressed n-PANI pellets. Electrical conductivity was measured by Ecopia Hall Effect Measurement System (Ecopia, HMS).

4. Result and discussion

4.1. FTIR

n-PANI was successfully prepared by mini-emulsion polymerization technique. The FTIR spectra of n-PANI prepared under the speed of 30000 rpm via homogenizer with 2 hours time reaction is shown in Figure 1. The main peaks consistent with C=N and C=C stretching vibrations of quinone and benzene ring [8] could be observed at around 1574 cm⁻¹ and 1489cm⁻¹ which confirmed the

presence of n-PANI [9, 10]. The peaks at 1372 cm^{-1} and 1291 cm^{-1} are attributed to the C-N stretching mode and the peak at 1114 cm^{-1} reveals the C-H bending vibrations [10].

4.2. XRD

Commonly, a polymer has an amorphous structure, however, n-PANI is showing crystalline structure due to their fibre nature and planar nature of benzenoid and quinoid functional groups [10]. Figure 2 shows the X-ray diffraction pattern of n-PANI emeraldine salt prepared under the speed of 30000 rpm via homogenizer with 2 hours time reaction forming three peaks. The characteristic peaks appeared at $2\theta = 14.8^\circ$, 20.5° and 25° , corresponding to (011), (020) and (200) crystal planes of PANI [8, 12]. These peaks are ascribed to the periodicity parallel and perpendicular to the polymer chains of PANI, respectively [13].

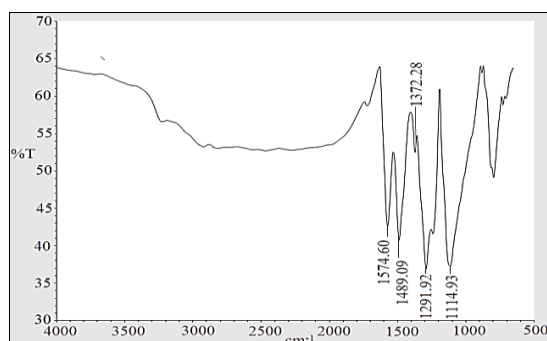


Figure 1. FT-IR spectrum of n-PANI

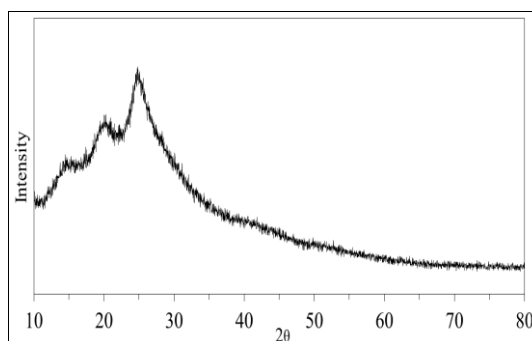


Figure 2. XRD diffractogram of n-PANI

4.3. Thermogravimetry analysis

Thermogravimetric analysis (TGA) of the n-PANI synthesized by mini-emulsion showed good stability at the higher temperature. Figure 3 shows thermogram of n-Pani prepared under the speed of 30000 rpm via homogenizer with 2 hours time reaction. The little weight loss in the initial stages around 6% is due to the volatilization of water and small molecules (oligomers and unreacted monomers) [14].

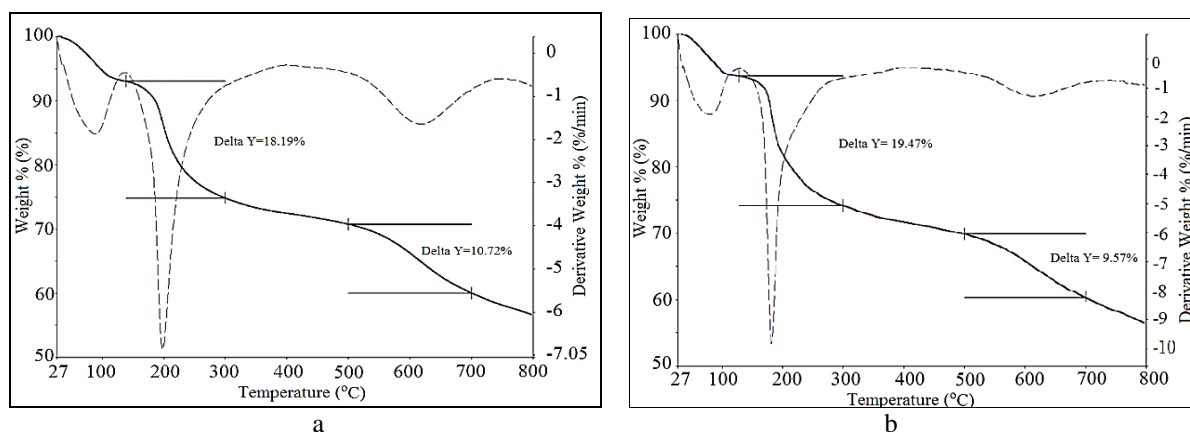


Figure 3. TGA thermograph of n-PANI a) without homogenizer b) with homogenizer

However, severe weight loss with a large slope occurring among $140\text{--}280^\circ\text{C}$ for PANI mostly originates from the dopant acid [15, 16]. The weight loss among $250\text{--}550^\circ\text{C}$ is caused by the degradation of the n-PANI main chain. The total weight loss at 800°C was around 60%. Both n-Pani prepared by the magnetic stirrer and homogenizer shows similar patent. However, for n-PANI prepared by the homogenizer, it gives extra weight loss at $140\text{--}280^\circ\text{C}$ may due to the higher amount of dopant acid it have compared to n-PANI prepared by magnetic stirring.

4.4. Morphology

The homogenizing effect on the morphology of n-PANI synthesized was investigated by FE-SEM. As shown in Figure 4, the nanofiber size between the polymeric aggregates is decreasing as synthesis temperature decreasing. In this way, an improvement of size due to the reducing of droplet size by homogenizer lead to a reduction of nanofiber size. Similar to TGA result, increasing of homogenizer speed may increase surface area by reducing of droplet size and results in an increment of the amount of dopant which related to the conductivity improvement.

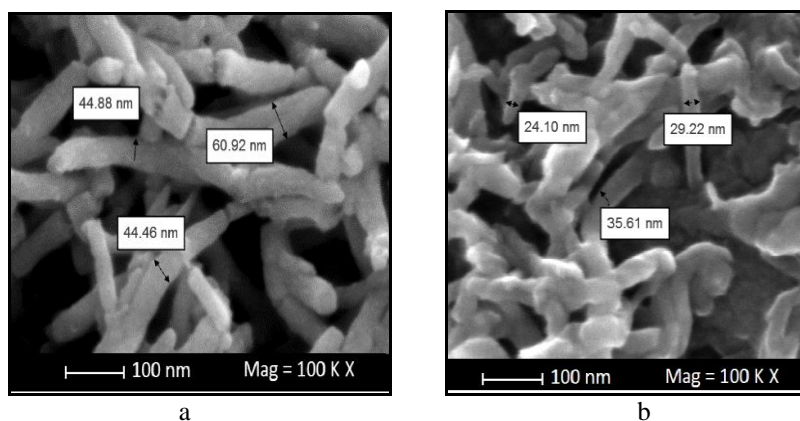


Figure 4. FESEM photograph of n-PANI a) without homogenizer b) with homogenizer

4.5. Electrical Conductivity

The electrical conductivity was measured by Hall effect technique. The influence of homogenizing effect on the conductivity as shown in Table 1 shows increasing of conductivity by increasing the homogenizer speed. The formation of nanofibers takes place in nucleation and initial growth stages. By applying high shear stress from homogenizer, the size of the droplet in nucleation step will decrease. Then the initial stage continues with smaller nucleation site which results in the formation of smaller nanosize compared to n-Pani without homogenizing effect. With the increasing formation of n-PANI nanofiber, which increased the dopant site resulting in increasing of electrical conductivity. Effect of time reaction on the electrical conductivity of n-PANI prepared using 30000 rpm of homogenizer speed is shown in Table 2. By the time of reaction, oxidation of emeraldine will reduce to completely polymerize. After 2 hours reaction, the electrical conductivity of n-PANI decreases and become stable up to 24 hours. It may explain by completely oxidized polyaniline that would be in the pernigraniline state. While reaction time less than 2 hours, aniline may not completely turn to emeraldine state which results to lower electrical conductivity.

Table 1. Effect of stirring speed

Speed(rpm)	Conductivity (Scm-1)	Size
Magnetic	5.2	55-65
10000	12.3	50-55
20000	15.9	35-40
30000	17.5	25-30

Table 2 Effect of time reaction

Time (Hour)	Conductivity (Scm-1)	Size
0.5	6.3×10^{-3}	25-30
1	1.5×10^{-2}	25-30
2	17.5	25-30
4	15.6	30-35
6	10.4	35-45
15	11.1	35-45
24	11.2	35-45

5. Conclusion

The (n-PANI) was successfully synthesized by mini-emulsion polymerization technique. The optimum speed and time reaction of the homogenizer for polyaniline polymerization to obtain the highest conductivity with reducing size of nanofiber is 30000 rpm in 2 hours. Electrical conductivity was strongly influenced by time reaction which longer period promotes to oxidation hence reduce the conductivity.

Acknowledgments

The authors greatly acknowledged the financial support by FRGS/1/2014/TK04/UKM/03/2 and GGPM-2014-027 from CRIM (Centre of Research and Instrument Management, UKM and KPT (Kementerian Pengajian Tinggi), Malaysia.

References

- [1] Hong Y, Hwang S, Yoon D S. and Yang J 2015 *Sensor Actua.t B-Chem.* **218**, 31–36.
- [2] Shamagsumova R, Porfireva A, Stepanova V, Osin Y, Evtugyn G and Hianik T 2015 *Sensor Actua.t B-Chem.* **220**, 573–582.
- [3] Marie E, Rothe R, Antonietti M and Landfester, K 2003 *Macromolecules*, **36**(11), 3967–3973.
- [4] Wang H, Wang L, Wang R and Tian X 2011 *J. Mat. Sci.* **46**(4), 1049–1052.
- [5] Elhalawany N, Elmelegy H and Nayfeh M 2015 *Synth. Met.* **205**, 145–152.
- [6] Stejskal J and Gilbert R G 2006 *Pure Appl Chem.* **74**(5) 857-867
- [7] Kumar A K, Mishra A, Awasthi K and Kumar V 2015 *Macromol. Symp.* **357**, 168–172
- [8] Abdolahi A, Hamzah E, Ibrahim Z and Hashim S 2012 *Materials*, **5**, 1487–1494.
- [9] Shao L, Qiu J, Liu M, Feng H, Lei L, Zhang G and Zhao Y 2011 *Synthetic Met*, **161**(9-10), 806–811.
- [10] Kavitha B, Prabakar K, Siva K, Srinivasu D, Srinivas C, Aswal V K and Siriguri V 2012 *IOSR J Appl Chem*, **2**(1), 16–19.
- [11] Vivekanandan J, Ponnusamy V, Mahudeswaran A and Vijayanand P S 2011 *Appl Sci Res*, **3**(6), 147–153.
- [12] Bhadra S and Khastgir D 2008 *Polym Test*, **27**(7), 851–857.
- [13] Srinivas C H, Srinivasu D, Kavitha B, Narsimlu N and Kumar K S 2012 *IOSR J Appl Phys* **1**(5), 12–15.
- [14] Mahmood W A K, Rahman K M M, Yeow Y G and Wee Y K 2012 *Int J. Chem Reac Eng*, **10**(1). 1-20
- [15] Masdarolomoor F 2006. *Novel nanostructured conducting polymer systems based on sulfonated polyaniline*. PhD Thesis. University of Wollongong. Australia
- [16] Wang Y, Chen K, Li T, Li H, Zeng R, Zhang R, Gu Y, Ding J and Liu H 2014 *Synthetic Met*, **198**, 293–299.