Crystallinity and Electrical Conductivity of PANI-Ag/Ni Film: The Role of Ultrasonic and Silver Doped

M Diantoro1,2, I N Fitriana1, F Parasmayanti1, Nasikhudin1, A Taufiq1,2, Sunaryono1,2, N Mufti1,2 and H Nur3

1Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang (State University of Malang), Jalan Semarang No 5, Malang 65145, Indonesia
2Center for Minerals and Advanced Materials, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang (State University of Malang), Jalan Semarang No 5, Malang 65145, Indonesia
3Centre for Sustainable Nanomaterials, Ibnu Sina Institute for Scientific and Industrial Research, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

Email: markus.diantoro.fmipa@um.ac.id

Abstract. Polyaniline (PANI) is typically a conductive polymer which has a uniqueness in structure and physical properties. The physical properties generally can be controlled by introducing a specific dopant as well as other processing parameters. This polymer has been widely investigated and applied in various fields, especially in electronics. Some metallic elements have been introduced to modified its characteristic such as iron and copper. In order to improve the characteristic of this material, it is important to study the optimum process as well as the elemental substitution of PANI films. In this study, we report the influence of employing sonochemistry technic and the silver substitution on the crystallinity and electrical conductivity of PANI/Ni films. The samples have been prepared similarly to the previous report with silver doped in the range of $0.1 \leq x \leq 0.5$ M. Other series of the sample were also prepared at various irradiation time of ultrasonic exposure. FTIR spectra showed that EB and ES Polyanilines had been successfully synthesized. X-RD histogram also revealed that crystallinity of the films comparably increased with the increase ultrasonic irradiation time as well as the silver in dopant. Along with the crystallinity, the electrical conductivity of films also increased as an increase of the dopant and of ultrasonic irradiation time.

Keywords: polyaniline, crystallinity, conductivity, sonochemistry, silver ion.

1. Introduction

The development of polymer materials engineering technology has found a wide range of materials that have certain advantages, one of which is a conductive polymer. The polymer which having an intrinsic electron conductivity appears to be an attractive organic semiconductor. These polymers have semiconducting properties associated with the availability of electron conjugation bond $-\pi$ which is a source of free charge in the polymer conjugation. The electron of unpaired $-\pi$ bonds, can move in conjugated carbon-carbon bonds of the polymer chain [1-3].

One of the most useful conjugated polymers to be used are polyaniline (PANI), which is characterized by the simplicity of synthesis, non-toxic, high sensitivity to external factors and its
potential as an optical material [4], high potential to be a good synthetic conductor [MacDiarmid]. Polyaniline is very promising for a variety of electronic applications, energy storage, pharmaceuticals and information technology. The basic form of polyaniline is the emeraldine base (EB), and emeraldine salt (ES) respectively the half-oxidized, and partially oxidized [1, 5].

Basically electrical conductivity or other physical properties of PANI can be improved by physical or chemical doping [5]. One way to do is adding a proton $H^+$ from HCl [2], CSA [6], iron, copper [7], lanthanum [8], nickel [9], cobalt [10] metallic ions, transition ions of arsenic [11], or other metal oxalates. So far the conductivity of PANI showed an increase with the increase of various dopants and other process parameters. However, the results showed that the range of conductivity was very large. There is also no detail information the relation between the dopant introduction, crystallinity and the electrical conductivity. The incomprehensive information shows no clear guidance of inferring microscopic mechanism in the material.

It is shown that the use of functional protonic acid such as CSA (camphor sulfonic acid) as a dopant, resulting PANI complex in conductive and non-conductive form soluble in the common solvents such as chloroform, xylene, m-cresol and others. Thus functional protonic acid allows conductivity of polyaniline can be processed as fiber, sheet, transparent thin films and others [5]. Some methods of coating films PANI-Ag / Ni is spin coating, screen printing, spray coating and so on [3]. The method used in this research is the spin coating method because of its advantages which can produce thin films with a thickness reaching nanometer scale. This process can also produce a homogeneous layer and relatively short time. The fabrication in the form of a thin film is very broad, because the properties of the material can be modified and close to application of devices. The combination of PANI and Ni as a substrate will give good results because it has a maximum conductivity, crystal quality, and high homogeneity because the Ni substrate has a high crystal orientation. So far there is no comprehensive study Ag dopants and ultrasonic irradiation with CSA on PANI on Ni substrate. Ultrasonic irradiation is not only intended as an enhancer of the PANI on conventional conductivity but also gives a chance to form nano and the crystalline phase of PANI-Ag/Ni. In this study, Ag nano has been used as a dopant into PANI/Ni film as well as the influence of ultrasonic irradiation to determine its conductivity.

2. Experimental Method
Two series of silver doped PANI-Ag/Ni and ultrasonic irradiation time films have been prepared using spin coating method. Each series was provided 5 samples. The basic configuration of PANI-EB and ANI ES were synthesized following the procedure of previous report [7]. The solutions of PANI-Ag had been prepared with synthesizing PANI-EB from aniline using the chemical oxidizing method. About 1.82 mL aniline (0.1 M) was dissolved into 50 mL HCl (0.2 M) liquid for about 1 hour. Along with this, a solution of 5.71 grams (NH$_4$)$_2$S$_2$O$_8$ (0.1 M) in 50 mL aquadest also prepared at the same time. After 1 hour, those two solutions just mixed and stirred a while then exposed at room temperature for about 24 hours for polymerization. The precipitated material was filtered using Whatman filter paper then washed using deionized water and aquadest until clean liquids observed. The obtained precipitated materials then mixed and homogenized using magnetic stirrer in NH$_4$OH (0.5 M) for 4 hours and then let them about 24 hours and washed using aquadest to obtain a blue PANI-EB. The powder of PANI-EB can be obtained after annealing the material for 5 hours at 80 °C. PANI-EB then mixed with the Camphor sulfonic acid (CSA) and then mixed with the AgNO$_3$ solution in chloroform and employing ultrasonic irradiation for various irradiation time. The obtained solution was filtered to obtain a PANI-Ag solution for deposition on nickel substrate using spin coating method. A different series of various AgNO$_3$ PANI doped of 0.1 M, 0.2 M, 0.3 M, 0.4 M, and 0.5 M also prepared in the same manner. The films have been deposited onto 1 x 1 cm$^2$ Ni substrate using spin coating method at 1000 rpm for 1 minutes. The obtained films then annealed at 100 °C for 1 minutes.

To check the formation of PANI-EB and PANI-ES (II), both series of the samples were characterized using FTIR and X-RD respectively to evaluate the bonds formation and crystallinity. X-
RD diffraction was conducted under Cu-Kα at 0.02 degrees of 2θ. The electrical conductivity measurement was conducted using the 4-probe method with 0.2 cm distance separated of the probes. Conductivity (σ) of the film was obtained by taking the reciprocal of its resistivity ρ which were obtained using the following Equation 1.

\[ \rho = \frac{2\pi s V}{I} \]  

Where ρ, V, I, and s expressed respectively of resistivity (Ωcm), voltage (volt), current (ampere), and probes’ distance.

3. Results and Discussion

Spectra of PANI-EB and PANI-ES(II) obtained from FTIR measurement is displayed in Figure 1. Basically, there are six main peaks showing the existing of functional groups of PANI-EB. The six peaks respectively appear at the wave number of 1581 cm⁻¹, 1489 cm⁻¹, 1377 cm⁻¹, 1303 cm⁻¹, 1151 cm⁻¹, dan 820 cm⁻¹[12] which are appear in the sample indicated by red bars in Figure 1.

![Figure 1. Transmittance (%) of (a) PANI EB and (b) PANI ES](image)

A strong peak at a wave number of 1593.2 and 1492.9 cm⁻¹ express the existing of C=N and C=C vibrations of quinoid and benzoid rings. The peak observed at 1300.02 cm⁻¹ shows a secondary aromatic amino C-N (–N–Benzoid–N–). The peak at 1147.65 cm⁻¹ indicated stretching mode of benzoid unit. The next peak at 1147.65 cm⁻¹ explains the existing electronic band or vibration of nitrogen quinoid (C=N stretching –N=quinoid=N–). A peak at 815 cm⁻¹ is originated from C–C and C–unit benzoid units which are used for indicating the key appearance of substituted benzene type. A typical of PANI-EB is the appearance of a strong peak at 1140 cm⁻¹ which is showing a vibration of quinoid nitrogen [14]. It means that the PANI-EB has been successfully synthesized. FTIR peaks of PANI-ES are closely similar to the PANI-EB. The main difference of the ES and EB spectra is the peak of a wave number in the area of 1593.2 cm⁻¹ and 1147.65 cm⁻¹ in which the EB spectrum appears very strong peaks which are not visible in the ES spectrum. This indicates imine C = N group at PANI-EB has turned into a form of amine C-N and -NH₂ in the PANI-ES.

Motomichi et al. [13] reported that the diffraction pattern for polycrystalline PANI exhibit Bragg’s peaks at 2θ of 5.2°, 9.5°, 15°, 20.9°, 25°, 27.5°, and 30°. Compare to the result of our pattern showed at Figure 2 shows that a strong peak exist at 5.2°. This peaks consistently appear at series of silver doped as well as time exposure of irradiation. A very strong peak at about 44° for different time irradiation
samples is belong to silver. A less strong peaks series shown by time irradiation PANI at 5° indicates that the film is more oriented than the silver doped PANI.

![Diffraction pattern of ultrasonic time (a) and silver doped (b) of PANI-Ag/Ni films](image)

**Figure 2.** Diffraction pattern of ultrasonic time (a) and silver doped (b) of PANI-Ag/Ni films

Theoretically, silver crystalline will appear at $2\theta = 44.08^\circ$. It is observed that the increase of silver ion doped give rise to a slightly shift to higher degrees. The respective peaks of 0.1 M, 0.2, 0.3, 0.4 0.5 M correspond to the appearance of the peaks at 44.30°, 44.32°, 44.30°, 44.28°, and 44.27°. The shift of the higher shift is correspond to the slightly decrease of silver particles. The substitution of silver ion is indicated also by the higher shift of the Bragg’s peaks.

Further analyses of the first peaks explore the relation between the dopant and irradiation time relative to the crystallinity. The crystallinity shows the degree of the crystal fraction in PANI-Ag/Ni as
well as the time irradiation PANI is shown in Figure 3. The crystallinity may play a key important role on the doped PANI and various time irradiation PANI for further examination of Figure 5.

![Graph](image_url)

**Figure 3.** Crystallinity PANI/Ni as a function of silver doped (a) and ultrasonic irradiation time (b).

SEM images of PANI-Ag films which were exposed under magnification of 10000 x showing a relatively similar morphology. At this magnification, the samples exhibit a homogenous surface. There is no crack, or another grain boundary fault appears on them. It looks that the grain or island are greater than 5 µm as shown by bar scale.

![SEM images](image_url)

**Figure 4.** SEM images of PANI-Ag/Ni films.

The crystallinity of the films shows an increase by increase of the dopant as well as the time of irradiation. As shown in Figure 3 the crystallinity was calculated from X-RD data is relatively low. This crystallinity can not be observed by SEM as depicted in Figure 4. For detail examination may be can be observed by TEM diffraction. Other important physical properties related to the dopant and the irradiation time of PANI is electrical conductivity. The electrical conductivity of both of the two series of samples is displayed in Figure 5.
Figure 5. Electrical conductivity at different silver doped (a) and irradiation time of sonochemistry (b).

It is observed that silver ion concentration, Figure 5(a) as well as irradiation time of ultrasonic, Figure 5(b) showing a similar trend i.e. increase the electrical conductivity. Even though they do not have a simple relation. The influence of silver ions PANI-Ag/Ni generally resulted electrical conductivity compare to the effect of irradiation time. The highest electrical conductivity achieved by 0.5 M silver doped sample which reaches up to 7.96 S/cm. This conductivity is higher than oriented PANI sample reported by Mihai [15] which reach 1 S/cm. On the other hand, this silver doped PANI/Ni is still lower than Ar’ and Ga’ doped PANI which was reported by Aleshin et. al [11] of 150 S/cm. This experimental data suggest that the prediction of MacDiarmid [1, 2] is revealed and potential to be studied further. Both of the crystallinity and conductivity obtained from this work is closely similar to the silver doped natural polymers [16].

4. Conclusion
In conclusion, we confirmed that the role of silver dopant, as well as the ultrasonic exposure, gives rise to increasing the crystallinity as well as the electrical conductivity. The electrical conductivity of PANI/Ni is higher than that of ultrasonic exposure. This result suggests that the silver doped can be used to improved the electrical conductivity in combination with CSA as well as ultrasonic irradiation.

5. References
[1.] MacDiarmid A G 2001 Synthetic Metals: A Novel Role for Organic Polymers (Nobel Lecture) Angew. Chem. Int. Ed. 40 2581 - 2590
[2.] Cristofolini L, Fontana M P, Konovalov O, Berzina T and Smerieri A 2009 Doping-Induced Conductivity Transitions in Molecular Layers of Polyaniine: Detailed Structural Study, Langmuir 25(21) 12429–12434
[3.] Stakhira P, Cherpak V, Volynyuk D, Hotra Z, Belukh V, Aksimentyeva O, Tsizh B and Monastyrskyi L 2010 Growth and Properties Of Conducting Polyaniine Thin Films Obtained By Means Of Ionic Sputtering In Crossed Electrical And Magnetic Fields, Rev. Adv. Mater. Sci. 23180-184
[4.] Saravanan S, Anantharaman M R, Ventachalam S, Avasthi D K 2008 Studies on the optical band gap and cluster size of the polyaniline thin films irradiated with swift heavy Si ions. Vacuum 82 56-60.
[5.] Stejskal J, Gilbert R G, Polyaniline. Preparation of a conducting polymer Pure Appl. Chem. 74 5 pp. 857–867, 2002
[6.] Mathew H, Punnaakal V S, Kuriakose S, Kumari B S, Manuel A.cy, Synthesis and Electrical Characterization of Polyaniline-Multiwalled Carbon Nanotube Composite with Different Dopants International Journal of Scientific Reserch Publication 3(8) 2013 1-10
[7.] Diantoro M, Purwaningtyas D, Muthoharoh N, Hidayat A, Taufiq A, Fuad A 2012 The Influence of Iron- and Copper-doped of PANi Thin Film on their Structure and Dielectric Properties *American Institute of Physics Proceedings* 1454. p268-271. 2012, Melville New York.

[8.] Krishna J B M, Saha A, Okram G S, Soni A, Purakayastha S and Ghosh G 2009 Electrical properties of polyaniline doped with metal ions *Journal of Physics D Appl. Phys.* 42 (9) 095404.

[9.] Tan Y, Zhang Y, Kan J 2009 Synthesis and properties on polyaniline in the presence of nickel chloride *eXPRESS Polymer Letters* 3 6 333-339.

[10.] Aghazadeh M, Aghazadeh F 2013 Electrical Conductivity Property Study of Polyaniline, Cobalt *Nanocomposite Journal of Applied Chemical Research* 7(3) 47-55

[11.] Aleshin A N, Mironkov N B, Suvorov A V, Usov I O, Co klin J A, Su T M and Kaner R B 1998 Conductivity and magnetoconductivity of Polyaniline films implanted with Ar$^+$ and Ga$^+$ ions near the critical regime of the metal insulator transition, *Journal of Physics: condensed matter* 10 (22) pp. 4867

[12.] Wallace G G, Geoffrey M S, Maguire K, Peter R 2009 Conductive Electroactive polymers *Intelligent Polymer System Perancis: CRC Pres.*

[13.] Motomichi I, Castillo-Ortega M, Michiko M, Inoue B 2011 Polyaniline Toluene sulfonates: X-Ray Diffraction and Electrical Conductivity. X-Ray Diffraction and Electrical Conductivity *Journal of Macromolecular Science 10.1080/10601329708011058.*

[14.] Nobuta T, Claire H et al 2009 Oriented Thin Film of PANI by Friction Transfer Method. *Mol. Cryst Liq Cryst* 505 pp 80-86

[15.] Mihai I, Addiego F, del Frari D, Bour J, Ball V 2013 Associating oriented polyaniline and eumelanin in a reactive layer by layer manner: composites with high electrical conductivity, *Colloids and Surface A: Physicochemical and Engineering Aspects 434(2013) 118-125.*

[16.] Diantoro M, Hidayati N N S, Latifah R, Fuad A, Nasikhudin, Sujito, Hidayat A 2016 Electrical Conductivity Modification of Extracted Jatropha Multifida L. and Pterocarpus Indicus Wild Latex Films *AIP Conference Proceedings 1719, 030034 (2016); doi: 10.1063/1.4943729.*

**Acknowledgments**

The authors would like to thank the DRPM, KEMENRISTEKDIKTI, Republic of Indonesia for providing the research grant for MD 2016-2017.