***Berkala Fisika*** **ISSN: 1410 -9662**
*Vol. 24, No. 3, Juli 2021, Hal. 93-99*

*Original paper*

# DETERMINATION OF THICKNESS AND OPTICAL BAND GAP OF POLYANILINE NANOFIBERS

**Ngurah Ayu Ketut Umiati[1], Evi Setiawati [1], Mochammad Facta[2]**

*[1]Departemen Fisika, Universitas Diponegoro Semarang*

*[2]Departemen Teknik Elektro, Universitas Diponegoro Semarang*

E-mail: ngurahayuketutumiati@lecturer.undip.ac.id

*Received: 18 Januari 2021; revised: 23 April 2021; accepted: 20 Juni 2021*

## *ABSTRACT*

*The study observed the thickness and optical band gap of polyaniline nanofiber (PNF). PNF in this study is synthesized by the interfacial polymerization method in Toluene Aniline 0.31 with the APS 4mmol dopant HCl solution with molarity between 1 M to 3 M. The synthesis results obtained were characterized by UV-Vis scanning spectrophotometer. The thickness and absorption coefficient (α) is observed by Swanepoel method and Beer–lambert's relation, respectively. The optical band gap is observed from extrapolation* $(\alpha h\nu)^2$ *versus* $h\nu$ *. The results of this study indicate that the molarity of dopants affect the thickness layer and optical band gap of the material.*

***Keywords:*** *polyaniline nanofiber, optical band gap, thickness*

## *ABSTRAK*

*Penelitian ini bertujuan untuk mengamati ketebalan dan celah pita optik polianilin nanofiber (PNF). PNF dalam penelitian ini disintesis dengan metode polimerisasi antarmuka dalam Toluena Anilin 0,31 dengan larutan APS 4mmol dopan HCl dengan molaritas antara 1 M sampai 3 M. Hasil sintesis yang diperoleh dikarakterisasi dengan spektrofotometer pemindaian UV-Vis. Ketebalan dan koefisien absorpsi (α) diamati masing-masing dengan metode Swanepoel dan hubungan Beer-lambert. Celah pita optik diamati dari ekstrapolasi* $(\alpha h\nu)^2$ *versus* $h\nu$ *. Hasil penelitian ini menunjukkan bahwa molaritas dopan mempengaruhi ketebalan lapisan dan celah pita optik bahan.*

***Kata kunci:*** *polianilin nanofiber,celah pita optic, ketebalan*

## INTRODUCTION

Polyaniline has been studied intensively because they have unique properties that environmental stability, thermal stability and good conductivity. This material has a doping protonic oxidation level, the nature and ions size in the polymer backbone affects the electronics range from insulators to conductors. As is known, Pani has completely basic reduced form leucoemeraldine base (LEB), half-oxidized emeraldine base (EB) and fully oxidized pernigraniline base (PB). LEB has the lowest energy absorption in the range of 320 nm, characterized by electronic transitions π-π* between the valence band and conduction. For EB absorption, energy range from 600 nm to contribute local on electronic transitions π-π* content transfer between the ring and the imine unit-phenyl-amine adjacent quinoid added intramolecular charge transfer exciton. Because of this character, emeraldine salt has the role of improving electrical conductivity. Various energy absorption at 320 nm and 530 nm PB are characterized by Peierls gap transition.

Along with the development of nanotechnology, nanostructured polyaniline has become a major focus in recent years. Nanostructured materials display unique and distinct properties, among others, (1) the grain size of nanoparticles is affected by the broad band-solid structure replaced by molecular-orbitals where the energy gap depends on the number of repeating structural units. These materials exhibit not only color-dependent size, but also the electrical behavior of the materials obtained by different synthesis methods. (2) The atomic size of the molecules in the nanomaterials results in a wider surface area.[3].

Interfacial polymerization is a polymerization technique that uses two reactive monomers. The two reactive monomers are dissolved in different solvents and then mixed, reacting at the interface between the two solutions. In the interfacial polymerization of aniline, the reaction uses aniline monomer dissolved in an organic solvent and the oxidant ammonium peroxydisulphate dissolved in an acid solution. The reaction product found at the interface of the two solutions is pure polyaniline nanofiber [4-6]. In the aniline polymerization reaction, an acid solution is required to increase the head-to-tail coupling between aniline monomers [7]. Usually, this aniline polymerization reaction uses strong mineral acids such as hydrochloric, sulfuric, nitric, perchloric or phosphoric. In the interfacial polymerization reaction, pure nanofibers can be produced by the reaction of mineral acids and organic acids such as formic, acetic, camphorsulfonic, methylsulfonic, 4-toluenesulfonic, ethylsulfonic or tartaric acid with aniline monomers.

The optical characterization of thin films provides information about band gap, energy gap, band structure, active optical defects etc. the optical band gap (Eg) and absorption coefficient can be evaluated from transmission or absorbance. The film thickness (t) and refractive index can be determined from the absorbance spectrum using the Swanepoel method [8, 9]. absorption coefficient is related to the extinction coefficient k, which is defined as the imaginary part of the refractive index (n) complex. In sensor applications, measurement of the optical properties of Polyaniline arises due to chemical interactions between analyte molecules and Polyaniline-based coatings. These measurements lead to changes in the optical absorbance spectrum, refractive index and thickness. Changes in these optical parameters indicate the optical sensor response, sensitivity and selectivity [10]. But it often becomes difficult because of the emergence of some solutions to get a rough idea of the thickness t and refractive index n.

The aim of this work is to determine the optical parameters of thin films of polyaniline nanofibers obtained by interfacial polymerization. Interfacial polymerization was carried out by varying the molar dopant of HCl. These optical parameters were extracted from the UV vis spectral data of the resulting thin film.

## EXPERIMENTAL DETAILS

### Materials

The materials used include; aniline ($C_6H_5NH_2$)- Merck, Hydrochloric Acid (HCl) – Smart Lab, Toluen ($C_7H_8$ atau $C_6H_5CH_3$) - Smart Lab, Aquadestilata, and Ammonium peroxydisulfate ($(NH_4)_2S_2O_8$) – Merck. All materials used are pure analysers.

### Synthesis

Polyaniline nanofiber was made from the interfacial polymerization between the aqueous phase (dopants, initiator and aquadest) and organic phase (toluena as organic solvent and aniline monomer). 0.32 M. Aniline 99.5% ($C_6H_5NH_2$) was added to toluene ($C_7H_8$) to get 50 ml organic phase (aniline-toluene). There are four mmol APS ($(NH_4)_2S_2O_8$) added to a solution of 37% HCl with molar concentrations in range of 1 M until 3 M to produce 50 ml water phase. Two solutions with different phase is mixed or combined and they were allowed to stand overnight to accomplish the polymerization. The results of precipitation polyaniline after polymerization was marked on the glass substrate.

### Characterization

The optical measurements of Polyaniline nanofibers were carried out at room temperature using Shimadzu UV-VIS scanning spectrophotometer in the wavelength range from 350 - 700 nm. Absorption spectra obtained by depositing nanofiber polyaniline on clean glass substrate. Swanepoel's envelope method was employed to evaluate the optical constants such as the refractive index $n$ and absorption coefficient $\alpha$ from transmittance spectra. The thickness of polyaniline nanofiber layer on substrat was determined from interference fringes of transmission data measured over the visible range.

## RESULTS AND DISCUSSION

Optical absorption spectra of polyaniline nanofibers in spectral range of 400 – 700 nm were recorded by using UV–Vis spectrophotometer. The analysis of the dependence of absorption coefficient on photon energy in the high absorption regions is performed to obtain the detailed information about the energy band gap of the films. The excellent surface quality and homogeneous layer conditions can be seen from the interferences fringers in the transmission spectra when the surface of the film reflects scattering / absorbing in most layers [9]. The optical constants were evaluated using the Swanepoel method [8]. Figure 1 shows the absorption spectra of HCl-doped polyanline nanofibers with molars varying from 1-3 M. The absorption spectra were plotted and analysed in the wavelength range of 400-700 nm. The absorption peaks appeared at wavelengths of 530 nm, 560 nm and 580 nm, respectively, in polyaniline with 1M, 2M and 3 M HCl dopant. This range of absorption peaks indicates an oxidized state of emeraldine [3].

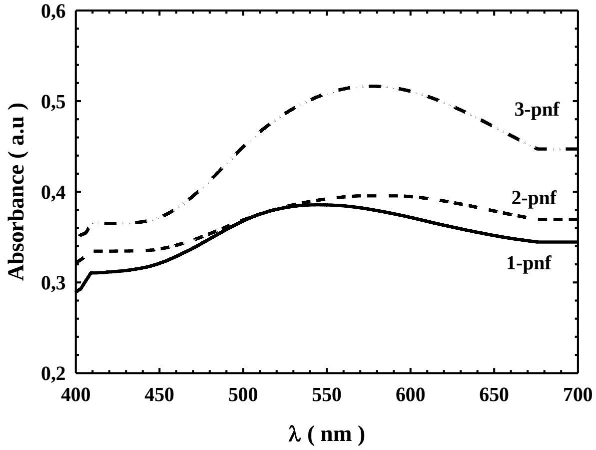

**Figure 1.** UV-Visible spectra of polyaniline nanofibers doped with 1 M HCl (1-pnf), 2M HCl (2-pnf) and 3 M HCl (3-pnf), respectively.

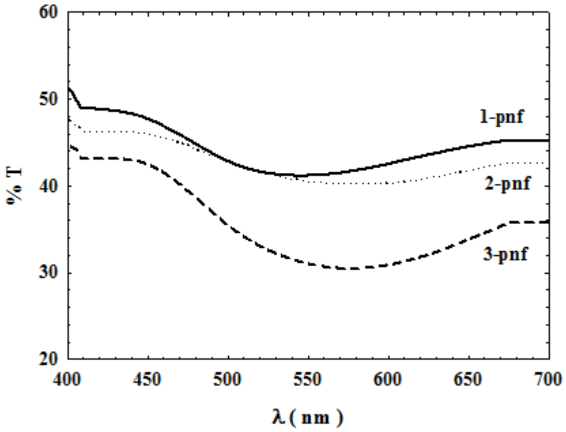

**Figure 2.** Transmittance spectra of polyaniline nanofibers doped with 1 M HCl (1-pnf), 2M HCl (2-pnf) and 3 M HCl (3-pnf), respectively.

## Determination of refractive index, thickness and absorption coefficient

Figure 2 shows the optical transmittance pattern of a layer of polyaniline nanofibers in the wavelength range of 400 – 700 nm. These results show that the transmission in the entire wavelength range decreases with the increase in the molarity of the polyaniline nanofiber. This is due to the high absorption layer associated with structural defects. The transmittance of the polyaniline nanofiber layer doped with HCl was 30%, 40% and 41% for 1M, 2M and 3M, respectively.

From the transmittance spectrum, the value of the refractive index and the thickness of the layer can be calculated using the Swanepoel method [8]. If $T_{max}$ ($T_M$) and $T_{min}$ ($T_m$) are the maximum and minimum transmittance values, s is the refractive index of the substrate (s = 1.52 for glass [11]), then the refractive index value of the coating can be calculated by

$$n = \left[N + (N^2 - s^2)^{1/2}\right]^{1/2} \qquad (1)$$

with

$$N = 2s\frac{T_M - T_m}{T_M T_m} + \frac{s^2+1}{2} \qquad (2)$$

If M is the number of oscillations between the two maximum and minimum conditions (if the oscillations occur consecutively then M=1), $n(\lambda_1) = n_1$ is the refractive index at the wavelength $\lambda_1$ and $n(\lambda_2) = n_2$ is the refractive index at the wavelength $\lambda_2$, then the thickness of a layer (t) can be calculated using the equation, following , [12]

$$t = \frac{M\lambda_1\lambda_2}{2(n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1)} \qquad (3)$$

$$t = \frac{\lambda_1\lambda_2}{2(n_1\lambda_2 - n_2\lambda_1)} \qquad (4)$$

From the calculation results obtained the value of the layer thickness of each molar variation of dopant as it is shown in Table 1.

**Table 1.** Thickness value (t) of Polyaniline nanofiber layer with dopant, molar variation.

| Dopant Molar Variation | t (layer thickness) |
|---|---|
| 1 M | 7.1 ± 0.2 μm |
| 2 M | 6.1 ± 0.2 μm |
| 3 M | 5.2 ± 0.4 μm |

Plotting the refractive index against wavelength can be seen in Figure 3 below. From the picture, it can be seen that the increase in the refractive index value is inversely proportional to the molar dopant, the higher the dopant molar, the lower the refractive index.

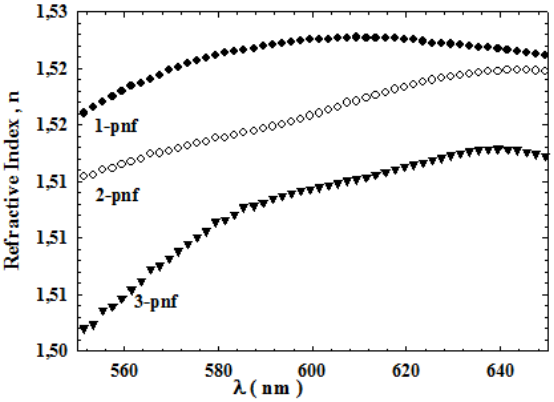

**Figure 3**. Plot of refractive index (n) against wavelength in the range of 550 nm – 650 nm.

The optical Absorption coefficient (α) can be calculated using the absorbance spectrum from the UV-Vis results. The absorption coefficient (α) can be calculated using the Beer–lambert's relation [11, 13],

$$\alpha = 2.303\frac{A}{t} \qquad (5)$$

where A, optical absorbance (from the UV-Vis absorbance spectrum), t layer thickness which is obtained from equation (4).

## Determination of optical band gap

For conductive polymers such as polyaniline, there are two distinct defect bands within the band gap. Two distinct defect bands arising from a destabilization of the highest occupied band (HOMO) and the lower defect band and a stabilization of the lowest unoccupied band (LUMO) leading to the highest defect band. Poyanilin has the doubly charged spinless bipolarons become unstable on a polyemeraldine chain resulting in the formation of two polarons, which separates to yield a polaron lattice. This results in the Pauli susceptibility increases linearly with the degree of protonation in Pani confirms the existence of a polaron lattice in Pani [14]. Thus, in Pani, instead of two bands, a single broad polaron band appears deep in the gap, which is also supported by band structure calculations [15].

The optical band gap can be determined using the Tauc relation [16], the direct band gap can be calculated by the equation,

$$\alpha h\nu = A\left(h\nu - E_g\right)^m \qquad (6)$$

$E_g$ is an optical exchange transition energy with absorption coefficient α and m is an optical exchange transition character with absorption coefficient. This transition character corresponds to the allowed characters, $m = {}^1\!/_2$ allowed direct, $m = 2$ allowed indirect, $m = {}^2\!/_3$ forbidden direct and $m = 3$ forbidden indirect. In this experiment, interfacial polymerization was carried out with molar variations of HCl dopants to obtain polyaniline nanofibers. The material formed is a nanostructure, electrons are simply transferred or transferred vertically from the top of the valence band to the bottom of the conduction band without changing the momentum/wave vector so when $m = {}^1\!/_2$ then equation (6), can be written as

$$\alpha h\nu = A\left(h\nu - E_g\right)^{{}^1\!/_2} \qquad (7)$$

$A$ is a constant, and $E_g$ is the optical energy gap for the direct transition. Values $E_g$ can be obtained by extrapolating $(\alpha h\nu)^2$ to the photon energy $h\nu$. Figure 4 shows the plot of $(\alpha h\nu)^2$vs $h\nu$ . This plot is linear over a wide range of photon energies indicating a direct type of transitions. The intercepts (extrapolations) of these plots (straight lines) on the energy axis reflect the energy band gaps. The optical band gap $E_g$ are given in Table 2. According to Table 2, a small difference occurred in the optical band gap.

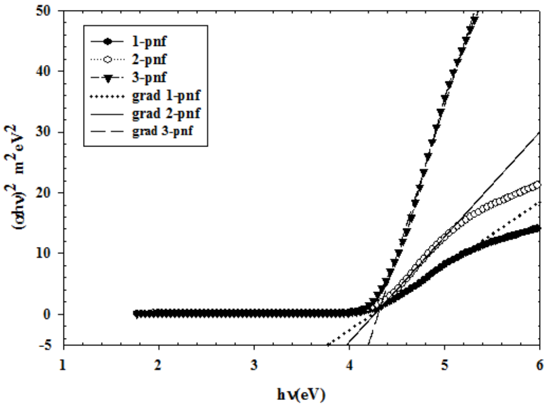

**Figure 4.** Plot against $(\alpha h\nu)^2$ vs $h\nu$ of polyaniline nanofibers with HCl dopant.

**Table 2.** Band gap value *Eg* of Polyaniline nanofiber layer with dopant molar molar variation

| Dopant Molar Variation | *Eg* (Optical Band Gap) |
|---|---|
| 1 M | 4.24 ± 0.01 eV |
| 2 M | 4.26 ± 0.01 eV |
| 3 M | 4.30 ± 0.01 eV |

## CONCLUSIONS

The study observed the thickness and optical band gap of PNF have been carried out. The synthesis results obtained were characterized by UV-Vis scanning spectrophotometer. The thickness and absorption coefficient (α) are observed by Swanepoel method and Beer–lambert's relation, respectively. The optical band gap is observed from extrapolation vs. The results of this study indicate that the molarity of dopants affect the thickness layer and optical band gap of the material. The larger the feeding molarity, the higher the optical band gap.

## REFERENCES

[1] Epstein A J, Ginder J M, Zuo F, et al. Insulator to - Metal Transition in Polyaniline. *Synthetic Metals*. 1987; 21(1-3): 63-70.

[2] McCall R P, Ginder J M, Leng J M, et al. Spectroscopy and defect states in polyaniline. *Physical Review B*. 1990; 41(8): 5202-5213.

[3] Singh P, Singh R A. Preparation and characterization of polyaniline nanostructures via a interfacial polymerization method. *Synthetic Metals*. 2012; 162(24): 2193-2200.

[4] Rezai F, Tavandashi N P, Zahedi A R. Morphology of polyaniline nanofibers synthesized under different conditions. *Res Chem Intermed*. 2014; 40: 15.

[5] Stejskal J, Gilbert R G. Polyaniline Preparations Of A Conducting Polymer. *Pure Appl. Chem*. 2002; 74(5): 857 - 867.

[6] Abdolahi A, Hamzah E, Ibrahim Z, et al. Synthesis of Uniform Polyaniline Nanofiber through Interfacial Polymerization. *Materials*. 2012; 5(8): 1487-1494.

[7] Huang J, Kaner R B. The intrinsic nanofibrillar morphology of polyaniline. *Chem. Commun*. 2006; 10(4).

[8] Swanepoel R. Determination of the thickness and optical constants of amorphous silicon. *J. Phys. E: Sci. Instrum*. 1983; 16(12): 1214.

[9] Caglar M, Caglar Y, Ilican S. The determination of the thickness and optical constants of the ZnO crystalline thin film by using envelope

method. *Journal Optoelectronics and Advanced Material*. 2006; 8(4): 1410-1413.

[10] Posudievsky O Y, Samoylov A V, Surovtseva E R, et al. Extraction of optical Constans of polyaniline thin films by surface plasmon resonance. *Thin Solid Film*. 2008; 516(18): 6104-6109.

[11] Ilican S, Caglar M, Caglar Y. Determination of the thickness and optical constants of transparent indium-doped ZnO thin films by the envelope method. *Materials Science-Poland*. 2007; 25(3): 709-718.

[12] Manifacier J C, Gasiot J, Fillard J P. A simple method for the determination of the optical constants n, k and the thickness of a weakly absorbing thin film. *J. Phys. E: Sci. Instrum*. 1976; 9(11): 1002.

[13] Gopalakrishnan K, Elango M, Thamilselvan M. Optical studies on nano-structured conducting Polyaniline prepared by chemical oxidation method. *Archives of Physics Research*. 2012; 3(4): 315-319.

[14] Huang W S, MacDiarmid A G. Optical properties of polyaniline. *Polymer*. 1993; 34(9): 1833-1845.

[15] Banerjee S, Kumar A. Swift heavy ion irradiation induced modifications in the optical band gap and Urbach’s tail in polyaniline nanofibers. *Nuclear Instruments and Methods in Physics Research B*. 2011; 269(23): 2798 – 2806.

[16] Tumuluri A, Naidu K L, Raju K C J Band gap determination using Tauc’s plot for LiNbO3 thin films. *International Journal of ChemTech Research*. 2014; 6(6): 3353-3356.