Synthesis of Conducting Polyaniline with Photopolymerization Method and Characterization

Siti Veren Joana Sury¹, Alizar Ulianas¹ and Syamsi Aini ¹
¹Departmen of Chemistry, Mathematic and Science Faculty, Padang State University, Padang, Indonesia

*alizar_chem@yahoo.co.id

Abstract. Polymers as they are known as molecules formed by repetition of small molecules known as monomers, polymers that are often used cannot conduct electricity. Along with the development of the polymer era at this time can also conduct electricity known as conductive polymers. One of the conductive polymers that attracts attention is polyaniline. Synthesis of polyaniline conductive polymers is carried out with aniline monomers mixed with Ethylene Glycol Dimetacrylate (EGDMA) as Crosslinkers, and Dimethoxy phenylacetophenone (DMPP) as the initiator. In this research, the polymerization process was carried out with a mixture of Aniline (mL), DMPP (0.1 g), and EGDMA (mL) polymerized with photopolymer. The polymers obtained were tested for electrical conductivity, the composition which showed optimum conductivity was in the ratio of aniline and EGDMA 1 : 1 with the electrical conductivity of 0.001462 Ohm.cm⁻¹. The conductivity measurement is done by using Four Point Probe (FPP) and other characterization measurements using FTIR (Fourier Transform Infrared) and TGA (Thermo-gravimetric Analysis).

1. Introduction
Polymers can be interpreted as a molecule formed by the repetition of small molecules known as monomers [1]. In recent years conductive polymers have attracted much attention because conductive polymers have unique thermal, electrical, and magnetic properties [2]. The conductive polymer is an organic polymer that can conduct electricity. Usually, the materials are semiconductive materials with electrical conductivity such as metals or metal oxides [3].

Conductive polymers can be applied as chemical sensors. Some conductive polymers that are often used for sensor materials include polypyrrole, polythiophene, and polyaniline [4]. Among these conductive polymers, polyaniline (PANI) is a polymer that is attracting a lot of attention because it has simple synthesis technology, has unique electrochemical characterization, and has good chemical and environmental stability [5]. Polyaniline is a polymer derived from aniline polymerization. Aniline monomers have the molecular formula C₆H₅NH₂ is one of the benzene derivatives, which one of the H atoms is replaced by the -NH₂ group and belongs to the amine group. Polyaniline and its derivatives can be used in various applications because it has a uniqueness that can be in three forms, namely leucoemeraldine, emerald, and pernigraniline. The most commonly used form is emeraldine salt (a semi-reduced and half-oxidized form) which has good stability.
Polymerization of aniline to obtain polyaniline is carried out using a very simple method, namely photopolymerization, which processes by mixing monomers (anilines), crosslinkers (ethylene glycol dimethacrylate), and initiators (dimethoxy phenyl acetophenone). This mixture will later be polymerized with a photopolymer for 600 seconds under a flow of nitrogen gas which the photopolymerization process also uses Ultra-Violet (UV) light to activate the monomer to become free radicals or ions for the start of the polymerization reaction [7].

The purpose of the research is to find out how the polymerization process of aniline by the method of photopolymerization and to determine the value of the electrical conductivity of polyaniline and its characterization of FTIR and TGA.

2. Research method

2.1 Aniline Polymerization Synthesis
Polyaniline synthesis was carried out using the photopolymerization method, in which 0.1 gram of weighed 2-2- Dimethoxy-2-Phenylacetophenone (Dmpp) purchased from Sigma-Aldrich was added to the volume ratio of aniline monomer purchased from Sigma-Aldrich and Ethylene Glycol Dimetacrylate (EGDMA) purchased from Sigma-Aldrich as shown in the following table.

| No | Aniline | EGDMA |
|----|---------|-------|
| 1  | 1 mL    | 1 mL  |
| 2  | 2 mL    | 1 mL  |
| 3  | 3 mL    | 1 mL  |
| 4  | 1 mL    | 2 mL  |
| 5  | 1 mL    | 3 mL  |
| 6  | 1 mL    | 4 mL  |
Each mixture of solutions was polymerized using ultraviolet light for 600 seconds under a continuous of nitrogen gas flow. Photopolymerization is the process of forming polymers using Ultra-Violet (UV) light to activate free radicals or ions for the initiation of the polymerization reaction in the nitrogen gas stream. Nitrogen gas is used in this process to expel other gases present in the photopolymerization chamber because the nitrogen gas is inert i.e. it does not react with the polymer base material.

2.2 Polyaniline Characterization

Polyaniline conductive polymers obtained will be tested by:

2.2.1 Electrical Conductivity (Four Point Probe). The obtained polyaniline will then be the carried out the electrical conductivity test, namely by using Four Point Probe (Fig. 3) with a distance of 0.2 cm each, and probes 1 and 4 are connected to the digital multimeter probes 2 and 3 connected to a digital multimeter. Data to be obtained from these measurements are the value of the voltage and output current. We called the measurement of four probes because it has four points of contact with the sample which have the same distance between the probes.

![Four Point Probe Tool Scheme](image)

**Figure 3.** Four Point Probe Tool Scheme

The conductivity of a material or sample can be determined by the relationship of the following equation:

\[ \text{Conductivity} = \frac{1}{\text{Resistivity}} \]  

(1)

With the:

\[ \sigma = \text{conductivity (Ohm.m)}^{-1} \]

\[ \rho = \text{resistivity (Ohm.m)} \]

While the resistivity determined by using the formula, bellows:

\[ \rho = 2 \pi s \left( \frac{V}{I} \right) \]  

(2)

With the:

\[ \pi = \text{radius value (3.14)} \]

\[ S = \text{distance between probes} \]

\[ V = \text{voltage value} \]

\[ I = \text{Strong current}[9] \]

2.2.2 Analysis of Fourier Transform Infrared (FTIR). The purpose of the analysis using FTIR is to identify the functional groups of a compound in polyaniline. Radiation from infrared often refers to the electromagnetic spectrum that lies between the visible region and the microwave region.
2.2.3 Thermo-gravimetric (TGA) analysis. TGA is a technique used to measure changes in the weight of a material as a function of time. The results of the analysis can be in the form of a continuous diagram where the decomposition reaction. The weight of a material needed when analyzed is several milligrams heated at a constant rate [10].

3. Results and Discussion

3.1 Electrical Properties Analysis (Four Point Probe)

The main purpose of this electrical properties analysis is to determine the electrical conductivity value of polyaniline conductive polymers, to know the conductivity value must first know the value of electrical resistivity. Conductivity and resistivity describe the good or bad of a material or sample in conducting electricity [11]. These electrical properties analysis is done by using a Four Point Probe (FPP) called the Four Point Probe because it has four points of contact with the sample that have the same distance between the probes. The distance between the 4 probes is 0.2 cm each, with probes 1 and 4 connected to the digital multimeter probes 2 and 3 connected to the digital multimeter, then the data to be obtained from measurements with these four probes is the value of the voltage and current output [12]. The value of polyaniline electrical conductivity can be calculated by equations 1 and 2.

| Aniline: EGDMA (mL) | Electrical Conductivity Value Ohm.cm⁻¹ |
|---------------------|---------------------------------------|
| 1: 1                | 0.001462                              |
| 2: 1                | 0.001227                              |
| 3: 1                | 0.001088                              |

Table 2. Value for electrical conductivity comparison of Anilin's volume with EGDMA

| EGDMA: Anilin (mL) | Electrical Conductivity Value Ohm.cm⁻¹ |
|--------------------|---------------------------------------|
| 2: 1               | 0.001058                              |
| 3: 1               | 0.001025                              |
| 4: 1               | 0.0009                                |

Table 3. Value of electrical conductivity comparison of EGDMA and Aniline volumes

From the following two images, the results of varying electrical conductivity, seen in Table 2, the value of electrical conductivity in aniline and EGDMA with a ratio of 1: 1 has a conductivity value which has a higher conductivity value than the others that is 0.001462 Ohm.cm⁻¹, this is due to the similarity of composition used both aniline and EGDMA so that aniline as its function can be maximized in providing maximum conductivity and EGDMA in crosslinking polymers. Furthermore, in the comparison of aniline with EGDMA 2: 1 and 3: 1 decreased the value of electrical conductivity that is 0.001227 Ohm.cm⁻¹ and 0.001088 Ohm.cm⁻¹, this can be interpreted that any addition of aniline volume with EGDMA volume can also still affect the the decrease in the value of electrical conductivity, of course this is due to EGDMA is no longer able to bind or connect components of aniline monomers into polymers as perfectly as they should function EGDMA as reinforcing or connecting polymer formation, this can also occur because EGDMA is a non-conductive compound, so more EGDMA will become a barrier for electron transfer to polyaniline polymers so that the conductivity value decreases. So that this also affects the polymer itself, which is the polymer produced a little softer and a bit more easily broken and this also affects the electrical conductivity value of polyaniline conductive polymers.
In Table 3, the optimum conductivity value is taken and then varied again to the EGDMA volume. So, there is a variation in the volume of EGDMA compared to the volume of aniline which has optimum conductivity value. Where in the comparison of EGDMA compared to aniline 2: 1, the conductivity value of 0.001058 Ohm.cm$^{-1}$ obtained was almost the same as the volume comparison of EGDMA compared to aniline 3: 1 also had an electrical conductivity value of 0.001025 Ohm.cm$^{-1}$. The results of these conductivity values sequentially have almost the same value but there is still a slight decrease in the value of electrical conductivity. Furthermore, in the latter comparison, EDGMA versus aniline 4: 1 decreased to the value of electrical conductivity that is equal to 0.0009 Ohm.cm$^{-1}$ this is due to the increasing number of EGDMA used as a polymer crosslinker making high cross-linking in the polymerization process and its conductivity ability decreased as well as reduced aniline volume and increasing EGDMA volume can also reduce the ability of aniline conductivity. The excess volume of EGDMA also makes the texture of polyaniline hard and easy to crack.

So, in these two images, a high conductivity value is obtained, that is in the ratio of aniline and EGDMA 1: 1 which has the same volume composition so that both are bonded together or crosslinked between the monomers with crosslinkers well so that sufficient conductivity results are found well.

3.2 Characterization of FTIR (Fourier Transform Infrared)

FTIR characterization was carried out on polyanilines as a result of synthesis, namely on polyanilines which had optimum electrical conductivity values. The results of the polyaniline conductive polymer test on Figure 4.

FTIR analysis results show that polyaniline has C-H, O-H, C = O, N-H, C-N, and C = C functional groups at various wave numbers. From the results of the FTIR there are characteristic bands of polyaniline at wave number 682.97 cm$^{-1}$ there is C-H indicating the existence of an alkene bond, at wave 752.03 cm$^{-1}$ it also indicates the presence of aromatic bonds (C-H). The N-H group is seen at a wave number of 3446. 82 cm$^{-1}$. At 3366.98 cm$^{-1}$, there was an O-H group, which is a carboxylic acid, as well as a wave number of 3226.63 cm$^{-1}$, and 2324.13 cm$^{-1}$ at this wave number, also showing the presence of a carboxylic acid or OH group. The characterization of polyaniline at a wave number of 1716.62 cm$^{-1}$ is a carbonyl strain (C = O) which states that polyaniline has covalent bonds and is electronegativity. Furthermore, the wave number of 1278.59 cm$^{-1}$ proves the existence of C-N groups from amines. Absorption at a wave number of 1616.35 cm$^{-1}$ shows the C = C (carbon double bond) group of the benzene structure in polyaniline. When seen from the C = C group that appears on polyaniline has a double bond. This bond is conjugated with the C-H, N-H, C-N bonds in polyaniline which makes polyaniline have polar properties. This is because each conjugated bond has different electronegativity abilities so that conditions like these cause polyaniline to become a conductive polymer.

![Figure 4. Polyaniline FTIR spectrum with optimum electrical conductivity values](image-url)
3.3 Characterization of TGA (Thermo-gravimetric Analysis)

The results of this TGA test on Figure 5.

![TGA Curve](image)

**Figure 5.** Polyaniline TGA curve with optimum conductivity

The results of measurements of thermal stability and its derivatives using TGA can be seen on the thermogram of polyaniline (Fig. 5). Mass reduction of polyaniline which is as much as 45.15% at 51.08°C - 165.40°C this indicates the occurrence of decomposition in polyaniline. Furthermore, at a temperature of 289.80°C - 330.61°C there was also a decomposition marked by a reduction in the mass of polyaniline around 24.44%, this process was endothermic. Another curve plot in the polyaniline sample which is also useful is to follow the thermal changes during cooling and heating in the polyaniline and polyaniline samples aimed at stability at temperatures around 50°C because at 50°C the polymer decomposition has not occurred.

4. Conclusion

Polyaniline is obtained from the synthesis of aniline monomers using the photopolymerization method. The synthesized polyaniline obtained had the highest conductivity value of 0.001462 Ohm.cm⁻¹. Comparison of Aniline and EGDMA volumes that have high conductivity values is 1:1.

Acknowledgment

Thanks to Padang State University for financial support via research operational grants SP-DIPA 023. 17. 2. 677514/2020.
References

[1] Bilmeyer, Fred W Jr. 1984. Textbook of Polymer Sciens 3rd Edition. USA: A Wiley Interscience Publication.

[2] Srinivas, C. (2012). Synthesis and Characterization of Nano Size Conducting Polyaniline. IOSR Journal of Applied Physic, 1 (5), 12-15. https://doi.org/10.9790/4861-0151215

[3] Winokur, MJ 1995. Model Calculations of Polaronic and Biopolaronic Defects in Li-Doped pi conjugated Polymers of Thiophene and Phenyl. Polaron, UK.

[4] Lange, U., Roznyatovskaya, UV and Mirsky. VM, 2008. Conducting Polymers in Chemical Sensors and arrays. Analytica Chimica Acta. 614, 1-26.

[5] Sun Zaicheng, et al. 1998. Ctalyc Oxidazation Polymerization of Aniline in an H2O2-Fe2 + System. Synthetic Metal.

[6] Pratt Colin. 1996. Conducting Polymers.

[7] Fouassier, JP, Allonas, X., & Burget, D. (2003). Photopolymerization reactins under visible light: principle, mechanism and examples of applications. Progress in organic coating, 47.1, 16-38.

[8] Wikipedia. 2017. Photopolymers. https://en.wikipedia.org/wiki/Photopolymer. Accessed on 24 November 2019.

[9] Schroder, K Dieter. 2006. Semiconductor Material and Device Characterization. Jhon Wiley & sons, Inc.

[10] Sembiring, S. 2014. Preparasi dan Krakterisasi Bahan. Buku Ajar Jurusan Fisika Universitas Lampung. Bandar Lampung

[11] Suyoso. 2003. Electric Magnet. Yogyakarta: FMIPA UNY. Pp. 44-50.

[12] Abdul, lim Mafahir., Tjipto Sujitno, and Ariswan. 2016. The Effect of Substrate Temperature on the Electrical Properties of Thin Layer Semiconductor Materials pbs, pbse, pbte Preparation Results by Vacum Evaporation Technique. Journal of Physics Volume 5, Number 2, pp. 137-147.