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Synthesis of Polyaniline Film via Vapor Phase Polymerization: Study of Effect of Temperature and Different Substrate on Film Conductivity

Tyara Salsabila Alicia Putri, Donatus Setiawan, Dwi Indarti and Bambang Piluharto*
Biomaterial Research Group, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Jember, Jalan Kalimantan 37 – Kampus Bumi Tegal Boto Kotak Pos 159 Jember 68121, Indonesia
*Corresponding author (e-mail: bampito.fmipa@unej.ac.id)

Polyaniline (PANi) is one of the promising conductive polymers due to easy to synthesis, environmental stability, and high conductivity. In its applications, PANi widely used as a material for electrochromic devices, light emitting diodes (LED), sensors and biosensors. However, existence conjugated structure in PANi form a rigid structure that makes it difficult to produce film. The aim of the research is to synthesis PANi using vapor phase polymerization (VPP) method and study of temperature effect and different substrates on the conductivity. The method comprises two steps, the first step of introducing the oxidizing agent in the substrate and second step, the polymerization of the vapor phase on the substrate. The polymerization temperature (45, 55 and 60 ºC) and the type of substrate (filter paper, bacterial cellulose, and cellulose acetate) were used as variables to study the conductivity properties. As the results showed that PANI has been successfully polymerized due to physical properties result and functional group analysis using FTIR. The effect of temperature treatment shows that increasing the temperature increases the conductivity value in the range of 10^{-5} up to 10^{-4} S/cm. Meanwhile, from various types of substrates, filter paper showed the highest conductivity compared to other substrates.

Keywords: Conducting polymers; polyaniline; polymerization; vapor phase; substrate

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Polyaniline (PANi) is one of the most widely studied conductive polymers because it has unique physical and chemical properties, so it has been widely developed in various applications (Rahayu et al., 2015). Polyaniline (PANi) has three forms based on the level of oxidation, namely pernigranilin, emeraldine, and leucomeraldin. Compare with the two others, emeraldin base have the most stable oxidation state. Emeraldin base is the most stable insulating form of polyaniline because its conductivity value can be adjusted from 10^{-10} S/cm to 10^{0} S/cm through an acid doping process (Maddu et al., 2008, Aini et al., 2016). However, existence conjugated structure in PANi form a rigid structure that makes it difficult to produce film. Therefore, to fix this disadvantages, modified on PANi,is needed to make a flexible material (William & Sitorus, 2014).

Flexible material based on PANi can be synthesized electrochemically to produce products in the form of films by Vapor Phase Polymerization (VPP) method. The method comprises two steps, the first step of introducing the oxidizing agent in the substrate and second step, the polymerization of the vapor phase on the substrate the concentration of monomer, polymerization temperature, time of polymerization, and the distance between the substrate to the monomer are factors that effect on conductivity and morphology of PANi (Kim et.al, 2007). The aim of the research is to synthesis PANi using vapor phase polymerization (VPP) method and study of temperature effect and different substrates on the conductivity.

MATERIALS AND METHOD

Chemicals

Cellulose acetate (CA) was purchased from Sigma Aldrich (MW 30,000, 39.9 wt%), aniline, dimethyl sulfoxide (DMSO) (Merck, =1.11 g/mL), dimethyl phthalate (DMP) (Schuchart, =1.19 g/mL), acetone (Merck, =0.79 g/mL pa), iron (III) chloride ($FeCl^3$) pa, NaOH pa (Merck) and methanol were purchased from Merck.

Instrumentations

Fourier Transform Infrared (FTIR. This analysis was carried out using the ATR technique and the spectra were recorded at a wavenumber of 4000-500 cm^{-1}. LCR meter was used to measure conductivity film.

Synthesis of Polyaniline by VPP Method with Different Substrates

The polymerization was carried out in this study using the *vapor phase polymerization* (VPP) method. The

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first step, the substrate (fuletr paper) soaked in 20 mL of $FeCl_3$ for 20 minutes then dried at room temperature for 1 hour. The dried substrate was placed in a device designed for vapor phase polymerization (VPP) in which it was filled with an aniline solution and then evaporated for 20 minutes. This study used variations in evaporation temperature, namely 45°C, 55°C and 60°C. The composite that had been successfully formed was then washed with ethanol and distilled water and then dried in the oven for 5 minutes at 60 °C. The dried samples were then stored in a desiccator. The same procedure was carried out for two others substrate (nata de coco (bacterial cellulose) and cellulose acetate).

The PANi/Cellulose Composite Film Conductivity Test

The PANi/cellulose composite film conductivity test was carried out using an LCR meter. Conductivity measurement using the board's 2-sided PCB with a surface area of 1,5 cm x 1,5 cm for clamping composite films. The composite that has been clamped to the PCB is then assembled with cables connected to the LCR meter. The LCR meter is set for resistance measurement (Ω).

FTIR Analysis

The analysis was carried by measuring using FTIR Nicolet iS10 ATR Diamond within spectral region of 400 – 4000 cm^{-1}.

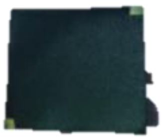
Morphology PANi/Cellulose-base Composites

Morphology composite was observed by Scanning electron microscopy with magnified 150 and 500 X.

RESULTS AND DISCUSSION

The synthesis of the PANi/cellulose composites was carried out using the VPP (Vapor Phase Polymerization) method with various cellulose-based substrates, namely nata de coco, filter paper, and cellulose acetate. The physical form of the substrate before the polymerization process and the PANI/cellulose composite after the polymerization process can be seen in Table 1.

Table 1. Physical Form of Substrate Before and after Polymerization Process.

Temperature (°C)	*Nata de Coco*	Filter paper	Cellulose Acetate
			
			
45			
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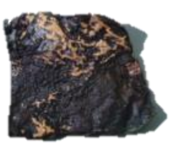
60			

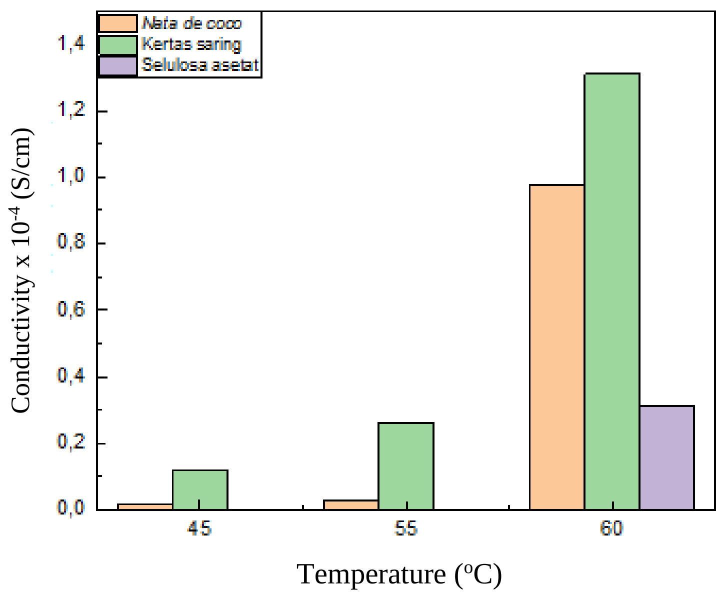


Figure 1. The conductivity value of PANi/cellulose composites (a) *Nata de coco*; (b) Filter paper; (c) Cellulose Acetate.

Table 1 shows the physical form of the substrate before the polymerization process and the PANi/ cellulose composite (filter paper, *nata de coco*, and cellulose acetate). The thickness of each of the three types of pure substrate was 0.062 cm, 0.073 cm, and 0.061 cm, respectively. After going through the polymerization stage and forming a PANi/cellulose composite (filter paper, *nata de coco* and cellulose acetate), each substrate had a thickness of 0.068 cm, 0.078 cm and 0.062 cm, respectively. The physical form of pure *nata de coco substrate* in the soaking process with $FeCl_3$ is very difficult to evenly absorb, in contrast to the results of soaking filter paper and cellulose acetate. This happened because the drying process of *nata de coco* caused the shape of the *nata de coco* substrate to shrink so that when the substrate was soaked with $FeCl_3$ only a little permeated and during the polymerization process with aniline monomer, the emeraldine salt of polyaniline formed in the *nata de coco substrate* was only slightly permeated to form an inhomogeneous green color. The next step is the polymerization process using the VPP method and the synthesis of each substrate with variations in evaporation temperature (45°C, 55°C and 60°C) produces a dark green PANi/cellulose composite as shown in Table 1.

Composite/ *nata de coco* as seen in Table 1, various polymerization temperatures (45ºC, 55ºC and 60ºC) difficult to produce a homogeneous dark green color. The Nata *de Coco* substrate when viewed from its physical form after the soaking process with $FeCl_3$ is a little difficult to absorb, so when the polymerization process using the VPP method at a temperature of 45ºC the reaction that occurs between $FeCl_3$ and aniline monomer has not formed an optimal emeraldine salt and produces a green color on the part. composite edge. This happens because, at a temperature of 45ºC $FeCl_3$ has not been maximally diffused on the nata de coco substrate.

Characterization

Effect of Evaporation Temperature of Aniline Monomer with Oxidizing $FeCl_3$ on Conductivity Value of PANi /Cellulose Composite Film

The conductivity value is obtained from the measurement of the resistance value (R) using an LCR meter. Measurement of the conductivity value of each PANi/cellulose composite (filter paper, *nata de coco*, and cellulose acetate) obtained the highest conductivity value at a temperature of 60ºC respectively, $1.31x10^{-4}$ S/cm, $9.75x10^{-5}$ S/cm, and $3.14x10^{-5}$ S/cm.

Figure 1 is a graph of the conductivity value of each PANi/cellulose composite (filter paper, *nata de coco*, and cellulose acetate). The higher the polymerization temperature used, the higher the conductivity value. Based on the graph above, the PANi/filter paper composite has a higher conductivity value when compared to the PANi/nata *de coco* composite and the PANi/cellulose acetate composite. This happens because the filter paper substrate is a type of cellulose that has good absorption, so that when viewed physically in Table 1, the PANi composite/filter paper produces a homogeneous green color. The PANi composite/filter paper from each polymerization temperature of 45ºC, 55ºC and 60ºC resulted in conductivity values of $1.18x10^{-5}$ S/cm, $2.6x10^{-5}$ S/cm and $1.31x10^{-4}$ S/cm, respectively. The three types of PANi/cellulose composites (filter paper, *nata de coco* and cellulose acetate) when compared at 45°C and 55°C the PANi/cellulose acetate composites do not appear on the bar chart because the conductivity values produced at these temperatures are very small when compared to the temperature of 60°C 7,07x10^{-9} S/cm, 1,08x10^{-8} S/cm and 3,14x10^{-5} S/cm, respectively. This happens because the cellulose acetate membrane when subjected to a heating process will reduce the pores of the membrane so that it will inhibit the aniline polymerization process using the VPP method. Kusworo *et al.* (2014) stated that the higher the heating temperature of the cellulose acetate membrane, the lower the flux value and the higher the rejection value of the membrane.

Functional Group Analysis of PANi/Cellulose Composites (Filter Paper, Nata de coco and Cellulose Acetate) Using FTIR (Fourier Transform Infrared)

The resulting PANi/cellulose composite synthesis was characterized by using FTIR to prove the presence of a typical peak that is owned by PANI. Figure 2 shows the spectra of each pure substrate, namely filter paper, *nata de coco*, and cellulose acetate. The spectra of each pure substrate were used to show the general cellulose absorption peaks so that they could be used as a comparison with the composite absorption peaks.

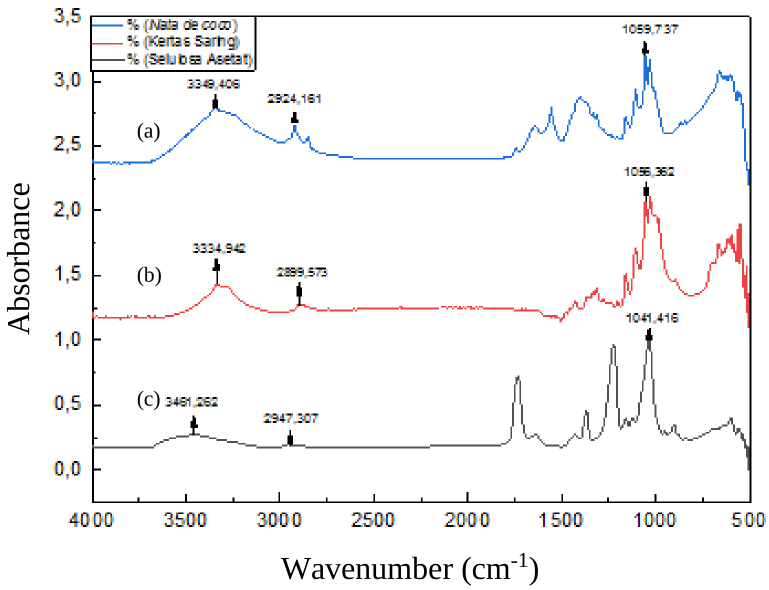


Figure 2. FTIR spectra of pure substrate (a) Nata de coco; (b) Filter paper; (c) Cellulose acetate.

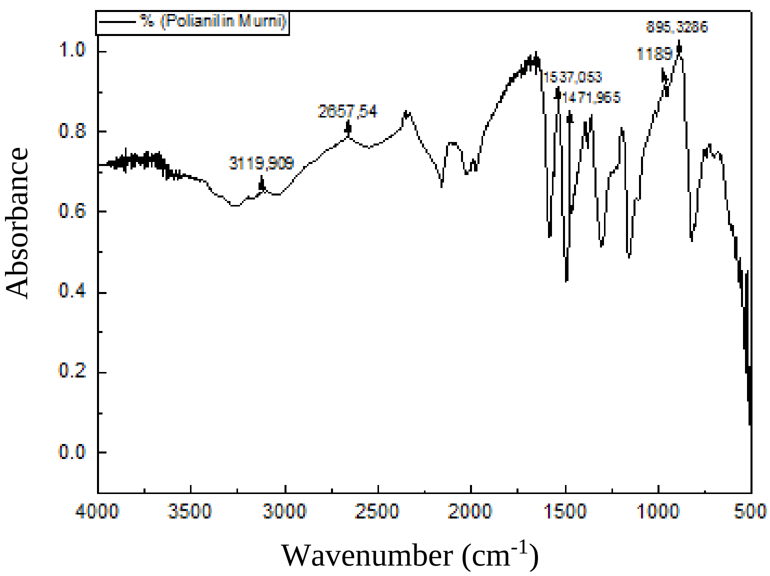


Figure 3. Pure Polyaniline FTIR Spectra.

The FTIR spectra in Figure 2 of each cellulose have a -OH stretching peak on *nata de coco* with a wave number of 3349,406 cm^{-1}, on filter paper with a wave number of 3334,942 cm^{-1} and on cellulose acetate with a wave number of 3461.262 cm^{-1}. Other absorption peaks that show the characteristics of cellulose are stretching vibrations on the C-H sp3 bond shown in nata de coco at wave number 2924,161 cm^{-1}, filter paper at wave number 2899,573 cm^{-1} and cellulose acetate at wave number 2947, 307 cm^{-1}. In addition, there are C-O-C ether vibrations which indicate the presence of glycosidic bonds between cellulose monomers, which are shown in nata de coco wave number 1059,737 cm^{-1}, on filter paper at wave number 1056,362 cm^{-1}, and in cellulose acetate at wave number 1041, 416 cm^{-1}.

Figure 3 is an FTIR spectra of pure polyaniline, which shows the characteristic peaks of polyaniline. The typical peaks of polyaniline are indicated by the wave numbers 3119.909 cm^{-1} representing N-H stretching, 1537.053 cm^{-1} representing the C=N stretching of the quinoid ring, at the C-N stretching of the benzoid ring at the wave number 1471.965 cm^{-1}, 895.3286 cm^{-1} representing the para-substitution C-H bond and the -NH•+= structure at the wave number 1189 cm^{-1}. Bhowmik *et al.* (2016) showed that the typical peak possessed by polyaniline, namely 3442 cm^{-1} representing N-H stretching, quinoid ring C=C stretching appearing at wave number 1560 cm^{-1}, 1642 cm^{-1} representing quinoid ring C=O stretching, 806 cm^{-1} representing para-substitution C-H bonds and the -NH•+= at wave number 1136 cm^{-1}. Based on these results, it can be stated that Figure 3 is polyaniline.

Figure 4 is the FTIR spectra of each PANi/cellulose composite at 60°C. Each PANi/cellulose composite (nata de coco, filter paper and cellulose acetate) found the characteristic peak vibrations possessed by PANi, namely stretching NH, C=C quinoid bonds, C-N benzoid bonds, C=N quinoids, C=C bonds. In the PANi-cellulose acetate composite, a C=O carbonyl group was also found. Kim *et al* (2007) stated that film formation and crystal growth of PANi will not grow at low temperatures <40°C, but film formation and crystal growth of PANi can occur at high temperatures of 50°C. At a temperature of 60°C, PANi/cellulose composites (nata de coco, filter paper and cellulose acetate) at a temperature of 60°C had a higher peak when compared to 45°C and 55°C. This happened because during the polymerization process, more aniline monomers evaporated so that more polyaniline was formed and, as a result, the spectral peaks were higher than the temperatures of 45°C and 55°C. The spectra of the three types of PANi/cellulose composites (filter paper, nata de coco, and cellulose acetate) showed a shift in wavelength, so that it can be said that there was an interaction between pure PANi and the substrate pure.

The morphology of the composite with various substrates (nata de coco, filter paper and cellulose acetate) is shown in Figure 5. Based on Figure 5 shows that the density of the fiber structure follows the following order: cellulose acetate > nata de coco > filter paper. The surface structure that is less dense for the filter paper causes the polymerization on the substrate to be optimal. This is good agreement with conductivity composites in different substrate.

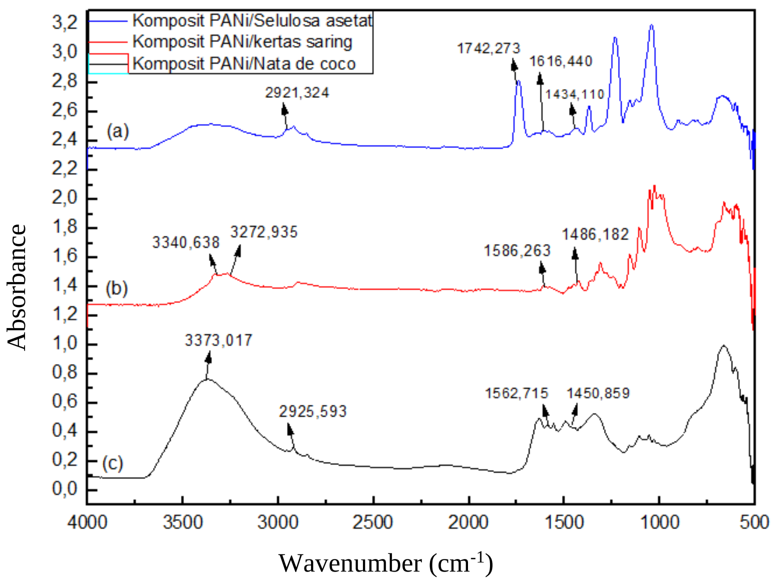
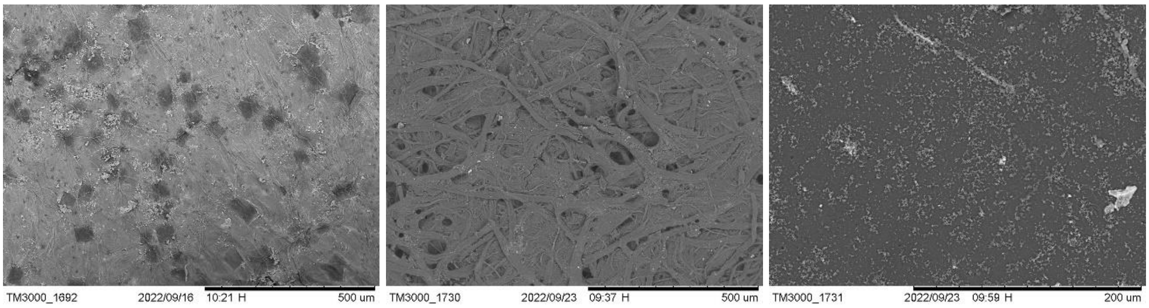


Figure 4. FTIR Spectra of PANi/Cellulose Composite (a) PANi /Cellulose acetate; (b) PANi/Filter paper; (c) PANi/ *Nata de coco* at 60°C.



(a) (b) (c)

Figure 5. SEM images of PANi loaded substrate: (a) Nata de coco (b) filter paper (c) cellulose acetate.

CONCLUSION

The composite of PANI film has been successfully prepared by vapor phase polymerization using various substrates. Increasing temperature of polymerization increase the conductivity value in the range of 10^{-5} up to 10^{-4} S/cm. Meanwhile, from various types of substrates, filter paper showed the highest conductivity compared to nata de coco and cellulose acetate.

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