SYNTHESIS OF POLYANILINE MICROCELLULOSE COMPOSITE

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ABSTARCT

SYNTHESIS OF POLYANILINE MICROCELLULOSA COMPOSITE. In this study, the Polyaniline-Microcellulose composite was produced as a solid electrolyte. In the previous research, polyaniline-cellulose composite has been carried out. However, the electronegativity and electrical voltage are still below the conventional batteries. In order to increase its performance, a polyaniline-microcellulose composite was synthesized. The purpose of this research is to determine the effect of the Polyaniline-Microcellulose composite on its conductivity and voltage values. Microcellulose synthesis used a combination method of sulfuric acid hydrolysis with concentrations of 30%-64% and sonication. Polyaniline - Microcellulose composite was synthesized via polymerization of aniline using chemical oxidation and sonication. Microcellulose was characterized using particle size analyzer (PSA). Microcellulose and PANI-microcellulose composites were characterized using FTIR, SEM-EDX, and XRD. The conductivity values and electrical quantities of PANI-Microcellulose composite were measured using LCR-meter and Digital Multimeter, respectively. The diameter of the microcellulose particles were between 20 nm – 40,6 µm. Microcellulose and PANI-Microcellulose composites showed identical absorption bands, namely the stretching vibrations to-OH and CH (aliphatic), which were shown at wavelengths 3444.87 cm⁻¹ and 2897.08 cm⁻¹, two typical groups of cellulose. The typical groups of PANI are bending vibrations from N-H, stretching vibrations of C=C, C-N, and quinoid ring C=N at wavelengths 1566.20 cm⁻¹, 1479.40 cm⁻¹, 1300.02 cm⁻¹, and 1141.86 cm⁻¹. PANI-Microcellulose composite morphology showed that PANI had been dispersed on microcellulose and free from impurities. The degrees of crystallinity are 30.9343% for microcellulose and 14.6079% for PANI-microcellulose. The optimum conductivity value of PANI-microcellulose composite at a ratio of 1:10 is 0.036013 S/cm; the electrical voltage is 1.34 volts with an electric current of 83 mA.

Keywords: Composite, conductivity, microcellulose, Polyaniline, sonication.

ABSTRAK

SINTESIS KOMPOSIT POLIANILIN MIKROSELULOSA. Pada penelitian ini diproduksi komposit Polianilin-Mikroselulosa sebagai elektrolit padat. Penelitian sebelumnya telah dilakukan sintesis komposit polianilin-Selulosa. Namun nilai elektronegativitas dan tegangan listrik masih dibawah nilai baterai konvensional, sehingga untuk meningkatkan nilai tersebut dilakukan sintesis komposit Polianilin-Mikroselulosa. Tujuan utama penelitian ini adalah untuk mengetahui pengaruh komposit Polianilin-Mikroselulosa terhadap nilai konduktivitas dan nilai tegangan listriknya. Sintesis mikroselulosa menggunakan kombinasi metode hidrolisis asam sulfat dengan konsentrasi 30%-64% dan sonikasi. Sintesis komposit. Polianilin – Mikroselulosa dengan polimerisasi anilin secara oksidasi kimia dan sonikasi. Mikroselulosa dikarakterisasi dengan PSA. Mikroselulosa dan komposit PANI-Mikroselulosa dikarakterisasi menggunakan FTIR, SEM-EDX, dan XRD. Komposit PANI-Mikroselulosa diukur nilai konduktivitas dan besaran listriknya berturut-turut menggunakan LCR-meter dan Multimeter Digital. Diameter partikel dari mikroselulosa 20 nm-40.6 µm. Mikroselulosa dan komposit PANI-Mikroselulosa menunjukkan adanya pita serapan yang identik yaitu terdapat vibrasi ulur terhadap –OH dan C-H (alifatik) yang ditunjukkan pada panjang gelombang 3444.87 cm⁻¹, 2897.08 cm⁻¹ yang merupakan dua gugus khas dari selulosa. Gugus khas dari PANI yaitu vibrasi tekuk dari N-H, vibrasi ulur C=C, C-N dan C=N cincin kuinoid yang terdapat pada panjang gelombang 1566.20 cm⁻¹, 1479.40 cm⁻¹, 1300.02 cm⁻¹, 1141.86 cm⁻¹. Morfologi komposit PANI-Mikroselulosa menunjukkan PANI sudah terdispersi terhadap mikroselulosa dan bebas dari pengotor. Derajat kristalinitas mikroselulosa 30.9343% dan PANI-Mikroselulosa 14.6079%. Nilai konduktivitas optimum komposit PANI-Mikroselulosa pada perbandingan 1:10 yaitu 0,036013 S/cm, tegangan listrik 1.34 volt dengan arus listrik 83 mA.

Kata kunci: Komposit, konduktivitas, mikroselulosa, polyanilin, sonikasi.

INTRODUCTION

The development of solid electrolytes currently uses inorganic materials, but it becomes a big problem because it cannot be processed naturally. Therefore, the material that has been developed is organic polymer material, namely polyaniline (PANI). PANI is one of the polymers that is often used because it has a high conductivity value and easily synthesized (Li et al., 2010). Polyaniline has the disadvantage of rigid material properties (William et al., 2014). To overcome the rigidity of polyaniline, a composite process was carried out using a microcellulose matrix (Adriani et al., 2013), because microcellulose has better and stronger mechanical properties as well as lower molecular weights than cellulose (Yani et al., 2017).

Synthesis of microcellulose commonly used is the hydrolysis of strong acids and sonication, because strong acids are able to chain, the isolation of microcellulose can remove the amorphous part of a cellulose (Oke, 2010). Composite processes to obtain high conductivity values included sonication treatment (Sitorus et al., 2011). The sonication treatment causes acid penetration in the microcellulose.

Therefore, the mixed aniline reacted better with acidified microcellulose. PANI polymerization worked optimally on the microcellulose portion, resulting in higher conductivity values (Sitorus et al., 2011). Previous research has been conducted by (Yuningsih, L. M., Mulyadi, D., & Sari, 2018), Synthesis of PANI-cellulose composites using the sonication method resulted in an optimum conductivity value of 0.00312 S/cm, and the resulting current is 71.4 mA with a potential of 1.31 volts. This value is still below the conventional battery value, which is 1.5 volts.

Based on the data and research that has been done above, a research on the synthesis of PANI- microcellulose composites was carried out in 2 steps. The first step was producing the microcellulose from corncobs by acid hydrolysis and sonication, characterized by PSA, FTIR, SEM-EDX, and XRD. The second step was producing solid electrolyte composite material which was done by dispersing microcellulose with polyaniline by sonication and dopant using HCl 3 M (Yuningsih et al., 2017). It was then characterized by FTIR, SEM-EDX, XRD, LCR-Meter and Digital Multimeter.

The purpose of this research is to make Polyaniline-microcellulose because the microcellulose in the composite process can increase the conductivity value, crystallinity (Schyr et al., 2014), surface area, and increased dispersion of composites (Ioelovich,

2012). The next purpose is to determine the conductivity value of the electrical quantity of PANI-Microcellulose composites, characterization of functional groups, morphology, crystallinity, and particle size of microcellulose.

MATERIALS AND METHODS

Materials

The materials used are corn cobs obtained from food vendors in the city of Sukabumi, and then aniline (Merck), potassium dichromate (Merck), sulfuric acid 95% (Merck), hydrochloric acid 37% (Merck), acetone, ethanol, sodium hydroxide, sodium hypochlorite (Merck).

Procedure

Isolation of Cellulose from Corn cobs

The method used in this work was similar to (Yuningsih et al., 2017). In brief, corn cobs chopped into small sizes, washed with water until clean. Then it was dried in an oven at 60°C for 24 hours. Corn cobs that have been dried are turned into powder using a grinding machine. The milled powder is then filtered in a size of 60 mesh.

The first step was delignification. 400 ml of NaOH 2% (w/v) was added to 16 grams of corn cobs powder. The mixture was refluxed at 90°C for 3 hours. The second step was bleaching; the resulting pulp was put into a 1% NaOCl solution at 70° C for 1 hour. The third step was the purification process; the result of bleaching was soaked for 30 minutes in 100 ml of 17.5% NaOH solution. The cellulose obtained was washed with distilled water and ethanol. Then it was dried in an oven at 60° C for 24 hours.

Synthesis of Microcellulose with Acid Hydrolysis and Sonication (Zeni & Favero, 2016).

1 gram of cellulose was added with 8.75 ml of H₂SO₄ with a concentration variation of 30%, 35%, 40%, 45%, 50%, 55%, 60%, and 64% (v/v), stirred at 45°C at a speed of 500 rpm for 30 minutes. The hydrolysis reaction was stopped by adding distilled water (1:15 v/v), and then it was left for 24 hours. The resulting solid was sonicated at 20 KHz and amplitude of 40% for 1 hour. Then, it was dried at a temperature of 45°C. The microcellulose was characterized by PSA, FTIR, SEM-EDX, and XRD.

Synthesis of PANI-Microcellulose Composite with Sonication (Yuningsih, L. M., Mulyadi, D., & Sari, 2018)

0.5 gram of microcellulose was sonicated with 75 ml of HCl 3 M for 1 hour. Then, aniline was added with weight ratios of microcellulose to aniline of 1:1, 1:5, 1:10, 1:15 and 1:20, and it was sonicated for 1 hour. $K_2Cr_2O_7$ was dissolved into HCl 3 M. The mol comparison of $K_2Cr_2O_7$ to aniline was 1:2. For 30 minutes the two solutions were mixed and stirred using a magnetic stirrer. After that, the mixture was left for 24 hours. The mixture was filtered using a Buchner funnel. The resulted composite was washed with 0.2 M hydrochloric acid 3 times, followed by C_3H_6O 100 ml. The composite was then dried at 60°C for 24 hours.

Characterization of Polyanilin-Microcellulose

The composite was characterized with Fourier Transform Infrared (FTIR) Spectroscopy to studied chemical structure. Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX) Spectroscopy was used to analyzed the morphology and the composition of the specimens. Than X-Ray Diffraction was used to measure the cristallinity. The conductivity and the electric quantities specimen both using LCR-Meter and Digital Multimeter.

RESULTS AND DISCUSSION

Cellulose Isolation

Based on the research results, the delignification step obtained the black filtrate because the presence of lignin was identified in the sample, hence the color of the filtrate changed from initially colorless (NaOH solution) to black. The results of the bleaching step obtained white cellulose, because the presence of hypochlorite ion as active bleaching agent can degrade the remaining lignin chains. Then the results of the purification step obtained pure cellulose is α -cellulose.

Synthesis of Microcellulose by Acid Hydrolysis and Sonication.

The synthesis of microcellulose in this study used a combination of methods between strong acid hydrolysis and sonication. The results of hydrolysis with sulfuric acid are shown in Table 1.

Table 1. Formation of microcellulose with Acid Hydrolysis Method

H ₂ SO ₄ Concentration	Microcellulose Result
30%	The Color is slight yellow, Crude fibre
35%	The Color is slight yellow, Crude fibre
40%	The Color is slight yellow, Fine

	fibre
45%	The Color is beige
50%	The Color is gray
55%	The Color is gray
60%	The Color is black
64%	The Color is black

Based on Table 1 sulfuric acid concentration from 45% to 64% cellulose colors are darker, due to burning suspension or carbonization. The optimum concentration of sulfuric acid is at 40% because the color of cellulose obtained was slight yellow and the cellulose fibers were fine.

Synthesis of PANI-Microcellulose Composite with Sonication

The interaction between microcellulose and aniline monomers in the synthesis of PANI-microcellulose composite was assisted by ultrasonic wave for 1 hour so that the aniline monomer entering the microcellulose fibers dissolved in HCl would form anilium ions.

Potassium dichromate ($K_2Cr_2O_7$) is an initiator in the aniline polymerization process. The result of polymerization for 24 hours was a composite mixture; some impurities which were reaction by products and residual monomers that were not finished reacting were dissolved in 0.2 M HCl and acetone (Stejskal & Gilbert, 2002).

Microcellulose PSA (Particle Size Analyzer) Measurement Analysis

The result of PSA analysis of particle size from microcellulose was 20 nm-40.6 with the cumulative result of particle diameter from corncobs' Microcellulose was 1561 nm. Number Distribution of measurement result with PSA is shown in Figure 1

Figure 1. PSA Measurement Result Graph

Fourier Transform Infrared (FT-IR) Analysis Spectrum of Microcellulose and PANI-Microcellulose Composites.

The FTIR result spectrums of microcellulose and PANI-microcellulose composites are shown in Figure 2.

Figure 2. FTIR Spectrum (a) Microcellulose (b) PANI-Microcellulose Composites.

Based on the microcellulose spectrum, there are a stretching vibration of -OH and a C-H (aliphatic) vibration indicated at the wave number 3444.87 cm^{-1} , 2897.08 cm^{-1} . The two functional groups are typical groups of cellulose. Other groups contained in cellulose are H-O-H, CH_2 , C-H (1,4 substituted by benzene) at vibrations of 1645.28 cm^{-1} , 1433.11 cm^{-1} and 894.97 cm^{-1} . Then C-O-C at 1163.08 cm^{-1} (Mohadi et al., 2014). PANI composite FTIR results showed that there are typical peaks of polyaniline, namely wave numbers 1566.20 cm^{-1} , 1479.40 cm^{-1} , 1300.02 cm^{-1} , and 1141.86 cm^{-1} , respectively are bending vibrations from N-H, stretching vibrations from C=C (Saikia et al., 2010), C-N stretching vibrations and quinoid ring C-N vibrations (Vollath & Szabó, 2004).

SEM-EDX (Scanning Electron Microscope-Energy Dispersive X- Ray) Analysis of the Microcellulose of PANI-Microcellulose Composites.

The morphology and composition of microcellulose and PANI-microcellulose composites were analyzed using SEM-EDX. The results of the SEM analysis are shown in Figure 3

Figure 3. SEM micrograms a) Microcellulose b) PANI-microcellulose composites

Based on Figure 8, the morphology of microcellulose undergoes agglomeration one after another. Then the PANI-microcellulose composite shows the surface of the microcellulose in the form of lumps (aggregate). According to (William et al., 2014) SEM image, the synthesized polyaniline emeraldine salt (PANI-ES) has a nanocrystal structure in the form of aggregate. The occurring aggregate was caused by a relatively high stirring and was formed because it was influenced by the drying process. In the drying process, water molecules were released constantly and caused the particles to be close together to form aggregates 2.

Table 2. Composition of Microcellulose Elements and PANI-Microcellulose composites 1:10

Sample	Element	Wt%
Microcellulose	Carbon (C)	50.78
	Oxygen (O)	49.22
PANI-Microcellulose	Carbon (C)	81.58
	Oxygen (O)	6.24
	Chlorine (Cl)	12.19

Based on the EDX results, Carbon (C) and Oxygen (O) in microcellulose and PANI-microcellulose composites are the constituent elements of cellulose. The Cl element contained in the PANI-Microcellulose composite is due to the addition of HCl doping. Thus, based on the EDX results, microcellulose and PANI-microcellulose composite are free from impurities.

XRD (X-Ray Diffraction) Analysis of Microcellulose and PANI-Microcellulose Composite

The diffractogram results of microcellulose and PANI-microcellulose composite are shown in Figure 4.

Figure 4. Diffractogram of Microcellulose (Blue) and PANI-Microcellulose Composite (Red).

Based on Figure 4, on the microcellulose diffractogram are peaks that appear in the areas $2\theta = 22.0016^\circ$, 20.2457° and 34.5845° which are the typical peaks of cellulose. The area $14-34^\circ$ is the typical peak of cellulose (Zhao et al., 2007). PANI-Microcellulose composite diffractogram gives typical peaks, which are in the areas $2\theta = 25.5350^\circ$ and 22.4855° . Diffraction peaks $2\theta = 20.42^\circ$ and 25.04° are structural characterizations of polyaniline emeraldine (Janaki et al., 2012). So, based on XRD diffractogram, it is known that PANI has been dispersed on microcellulose.

PANI-Microcellulose Composite Conductivity Values and Electrical Quantities

PANI-Microcellulose and PANI-cellulose composite conductivity values are shown in Table 3.

Table 3. Conductivity Values of PANI-cellulose Composite (Yuningsih, L. M., Mulyadi, D., & Sari, 2018) and PANI-Microcellulose Composite

Composite	Conductivity Value (S/cm)				
	1:1	1:5	1:10	1:15	1:20
PANI-Microcellulose	1.9291×10^{-3}	1.7826×10^{-2}	3.6013×10^{-2}	5.9965×10^{-3}	1.0629×10^{-2}
PANI-Cellulose	2.82×10^{-6}	1.53×10^{-6}	2.31×10^{-3}	3.12×10^{-3}	2.25×10^{-3}

Based on the weight ratio of microcellulose to aniline, the optimum conductivity value of PANI-Microcellulose composites is at 1:10 ratio, which is 3.6013×10^{-2} S/cm, producing a voltage of 1.34 volt with a current of 83 mA, while that of PANI-Cellulose composite is at 1:15 ratio, which is 3.12×10^{-3} S/cm, and the electrical voltage is 1.31 volts with a current of 71.4 mA. The conductivity value of PANI-Microcellulose composite is the highest at ratio of 1:10, while that of PANI-Cellulose composite is the highest at ratio of 1:15. This is because microcellulose is smaller than cellulose, thus, aniline added in small amounts has been completely dispersed, whereas in cellulose aniline added must be in large amounts to be completely dispersed.

The conductivity values and electrical quantities of PANI-microcellulose composite are greater than those of PANI-cellulose composite, because a material with smaller particle size will provide greater volume and surface area, so polyaniline sticks a lot in microcellulose, and results in greater conductivity values (Abdullah et al., 2008).

CONCLUSION

Based on the research results, the corn cobs' microcellulose particle diameters are between 20 nm – 40.6 µm. The highest conductivity value is owned by PANI-Microcellulose composite with optimum conductivity value at 1:10 ratio, namely 3.6013×10^{-2} S/cm. The functional group analysis of Microcellulose and PANI-Microcellulose composite showed identical absorption bands, namely stretching vibrations towards –OH and C-H (aliphatic) shown at wavelengths 3444.87 cm^{-1} and 2897.08 cm^{-1} , two typical groups of cellulose, and also typical groups of PANI, namely bending vibrations of N-H, stretching vibrations of C=C, C-N and quinoid ring C-N located at wavelengths 1566.20 cm^{-1} , 1479.40 cm^{-1} , 1300.02 cm^{-1} , and 1141.86 cm^{-1} . The morphology of PANI-Microcellulose composite showed that PANI has been dispersed and free from impurities. The degrees of crystallinity are 30.9343% for microcellulose and 14.6079% for PANI-microcellulose.

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