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Effect of Swelling and Sonication Methods on Conductivity of Polyaniline-Cellulose from Corn Cob (Zea mays L.)

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Abstract

The material of polyaniline conductive was synthesized with various pretreatment swelling method, sonication, and a combination of both methods on cellulose to form PANI-cellulose composites. Matrix cellulose isolated in corn cob by delignification method with NaOH and NaOCl solutions. Potassium dichromate was used as an initiator on oxidative polymerization of aniline. Characterization of PANI-Cellulose composite was draw using FT-IR and SEM, while the conductivity and electric quantities both using LCR-meter and digital multimeter. FT-IR spectra and SEM showed that PANI-Cellulose has been synthesized successfully by swelling, sonication, and combination of both methods. The PANI-cellulose composite with sonication method has the highest electrical conductivity 0.00312 S/cm with the voltage 1.31 volt.

Keywords: cellulose, composites, conductivity, sonication, swelling

INTRODUCTION

The research of developing conductive materials is done until now. The development of batteries from organic compound is an alternative choice because it has many advantages, one of which is environmentally friendly. The inorganic compound such as Ni batteries, Ni-Cd and Li-Ion batteries have been the problem because batteries cannot be processed naturally. Making a battery using an organic compound can be used as an alternative to [1].

Development methods were carried out to obtain high conductivity values using the swelling method [2] and the sonication method [1]. The swelling process using DMSO solution to break hydrogen bonds and activate hydroxyl groups in cellulose. Aniline can penetrate cellulose [2]. Sonication treatment will increase polymer conductivity.

The responsible swelling process will make the acid penetrate each part of the cellulose, so that the added aniline will be better to use acidified cellulose. PANI polymerization takes place optimally in the part of cellulose and results in higher conductivity [1].

In this study the swelling and sonication method of PANI-Cellulose composites synthesized from corn cobs was carried out to obtain a higher conductivity value, then characterized used in the form of functional groups, conductivity, morphology, and composition as well as electrical quantities using FTIR, LCR-metre, SEM-EDX and Digital Multimeter.

EXPERIMENTAL

Material

The materials used are cellulose synthesized from corn cobs, sodium hydroxide, sodium hypochlorite, ethanol, aniline, DMSO, potassium dichromate, hydrochloric acid, and acetone.

Cellulose Isolation [3]

400 mL NaOH 2% solution was added to 16 grams of corn cobs powder. The mixture was refluxed at 90^{o}C to produce pulp for 3 hours. The next step is the bleaching step, the resulting pulp is put into 1% NaOCl solution at 70^{o}C for 1 hour. In the purification process, the residue from bleaching was soaked in 100 mL NaOH 17.5% solution for 30 minutes. The cellulose obtained was washed with distilled water and ethanol. The cellulose washed was dried at 60°C in an oven for 24 hours.

Synthesis of PANI-Cellulose Composite without Swelling and Sonication

0.5 grams of cellulose was added to aniline. The weight ratio of cellulose and aniline is 1: 1, 1: 5, 1:10, 1:15, and 1:20. 75 mL HCl 3 M solution was added into the mixture of aniline-cellulose. $K_2Cr_2O_7$ was dissolved in 75 mL HCl as the initiator solution. The mole ratio of the initiator and the monomer is 1: 2. The solutions mixed and kept stirred for 30 min and then the polymerization process for 24 h. The polymerization results were filtered and washed with HCl and acetone then dried in the oven at 60^{o}C for 24 h.

Synthesis of PANI-Cellulose Composite with Swelling [2].

0.5 grams of cellulose was swelling in 35 mL of DMSO for 1 h. Aniline is added to the mixture with a variation of the weight between cellulose to aniline is 1: 1, 1: 5, 1:10, 1:15, and 1:20. The mixture kept stirred for 1 h using a magnetic stirrer. The mixture was added 75 mL of HCl 3M solution and continued with the addition of an initiator. The mole ratio of an initiator ($K_2Cr_2O_7$) to the monomer is 1: 2. The mixture kept stirred for 30 min then the polymerization process for 24 h. The polymerization results were filtered and washed with HCl and acetone then dried in the oven at 60^{o}C for 24 h.

Synthesis of PANI-Cellulose Composite with Sonication [2].

0.5 grams of cellulose was sonicated with 75 mL of HCl 3M for 1 hour. Aniline added with a variation of the weight between cellulose to aniline 1: 1, 1: 5, 1:10, 1:15, and

1:20. The mixture was sonicated for 1 hour. The mole ratio of an initiator ($K_2Cr_2O_7$) to the monomer is 1: 2. The mixture kept stirred for 30 min then the polymerization process for 24 h. The polymerization results were filtered and washed with HCl and acetone then dried in the oven at 60°C for 24 h.

Characterization of PANI-Cellulose

The chemical structures of the PANI-Cellulose composites were studied using Fourier Transform Infrared (FTIR) spectroscopy. Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy was used to analyze the morphology and the composition of the specimens. The electrical quantities and the conductivity of specimens both using Digital Multimeter and LCR-Meter.

RESULT AND DISCUSSION

Cellulose Isolation

Isolation of cellulose was synthesized from corn cobs by three step. The step is delignification (pulping), bleaching, and purification. The delignification step purpose is to degrade lignin in the corn cobs. Lignin can dissolve in an alkali solution and is easily attacked by oxide substances [4]. NaOH solutions can impair the lignin structure and separate part of hemicellulose [5].

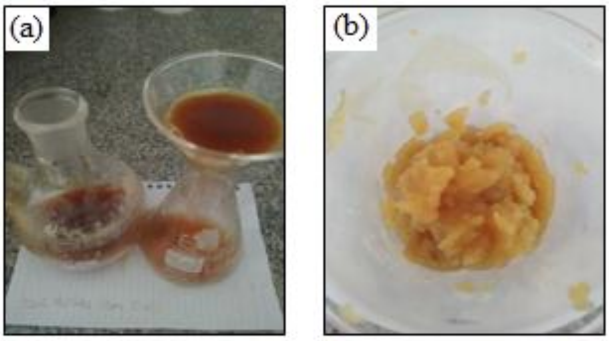

Figure 1. (a) Delignification (b) filtration results

The mechanism of break lignocellulose bonds with NaOH is shown in Figure 2.

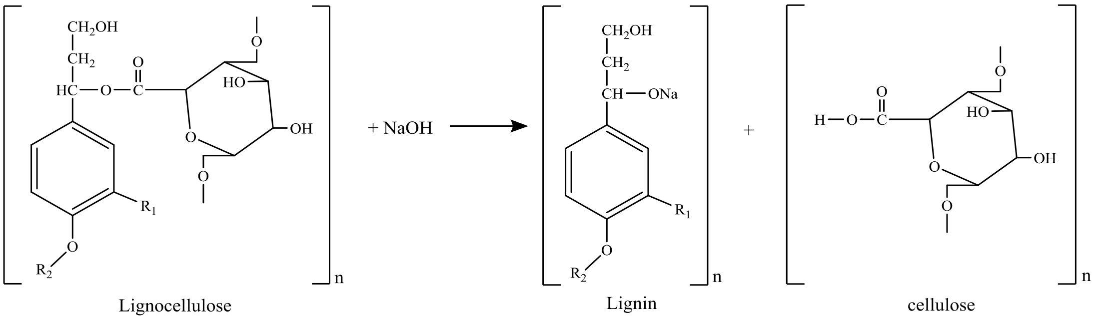

Figure 2. The reaction of break lignocellulose bonds with NaOH [6]

Lignin residual after delignification step can be removed by the bleaching step [7]. The bleaching step purpose to obtain brightness, improve and minimize degradation of cellulose fibers [8]. In this step degradation of the lignin residual chain occurs. Ion hypochlorite is an active whitening agent [6].

According to research [7], the chromophore residue is oxidized to polar compounds and easily dissolves in water. The reaction of lignin oxidation in the bleaching process can be seen in Figure 3.

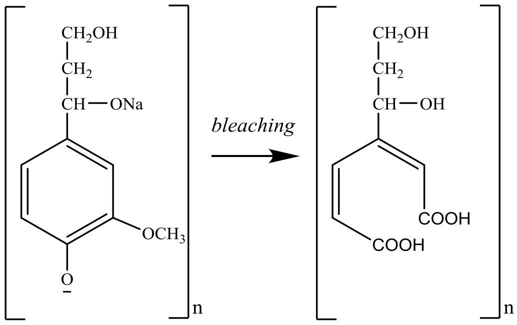

Figure 3. The reaction oxidation of lignin in the bleaching step [7]

The α-cellulose purification step uses 17.5% NaOH to obtain α-cellulose. α-cellulose is a long chain cellulose which is insoluble in 17.5% NaOH solution while β-cellulose and γ-cellulose dissolve in 17.5% NaOH or strong bases because β-cellulose and γ-cellulose have a short chain. [9]. Cellulose produced by corn cobs isolation in the form of white fibers.

SYNTHESIS OF PANI-CELLULOSE

Synthesis of PANI-Cellulose composites is carried out by polymerizing aniline by chemical oxidation on the cellulose matrix. The interaction between cellulose and aniline monomer is assisted by stirring for 30 minutes so the aniline monomers can penetrate to the cellulose surface fibers. Aniline is dissolved in HCl will form anilinium ion. Anilinium ion formation made polymerization reactions to be more optimal.

Potassium dichromate in acidified aqueous solution produces chromic acid [10]. In the initiation step, chromic acid withdraws one electron from each protonated aniline and forms a metastable complex. The complex undergoes dissociation and forms aniline cation radical. The propagation step, the transfer of two electrons from two radical aniline ions by H_2CrO_4 produces the semidine and H_2CrO_3. Cr (IV) oxidizes semidines to Pernigraniline Salt (PS) quickly. The color of the solution will be blue due to the formation of PS. The termination step, the aniline residue in the solution will reduce Pernigraniline Salt (PS) to Emeraldine Salt (ES) when all the oxidants have reacted. The color of the solution will be a green due formation of ES.

Characterization of PANI-Cellulose

PANI-Cellulose Functional Group

The results of FTIR cellulose spectrum from the isolation of corn cobs and PANI are shown in Figure 4

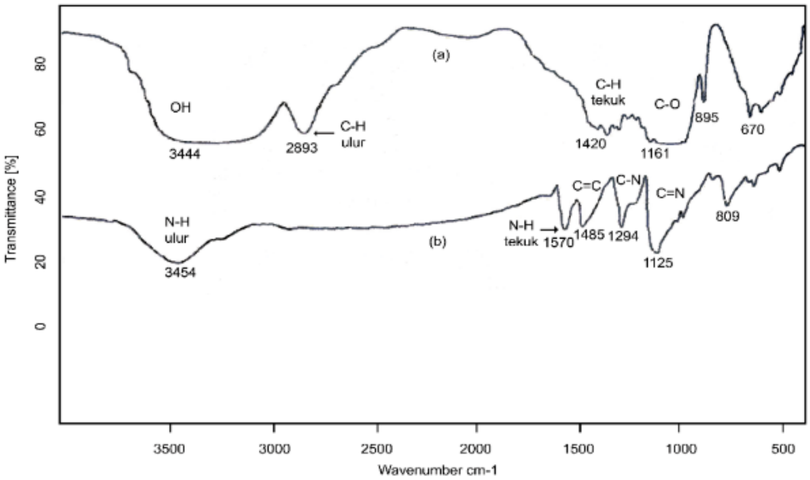

Figure 4. FTIR spectrum (a) cellulose from corn cobs [3] (b) PANI [11].

In a spectrum, the band appeared at 3444 cm^{-1} due to –OH stretching and at 2893 cm^{-1} to the C-H stretch vibration and bending vibration of C-H are shown with characteristic peaks at 1420 cm^{-1}. The C-O stretch vibration peak at 1161cm^{-1} and a peak of 895 cm^{-1} were assigned as a vibration of C-H (1,4 substituted by benzene) [12].

The PANI-Cellulose composite FTIR spectrum results are shown in Figure 5.

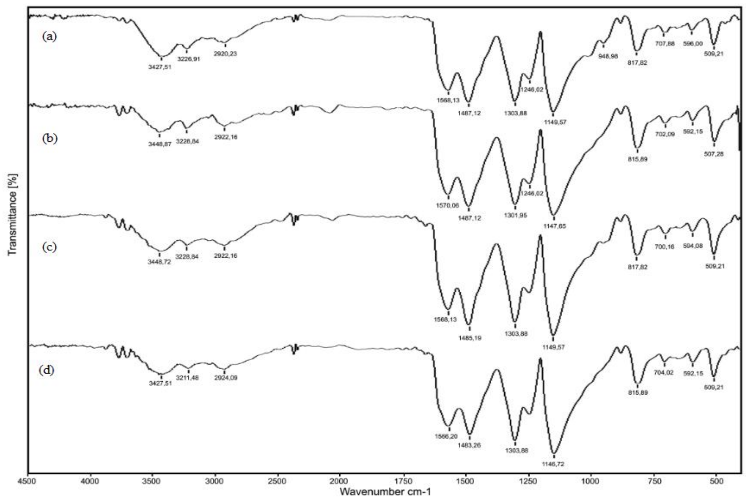

Figure 5. PANI-Cellulose composite FTIR spectrum (a) without swelling and sonication methods (b) swelling and sonication methods (c) swelling method (d) sonication method

Based on Figure 5 it can be seen that there are several absorption peaks of the PANI-Cellulose composite structure characteristics. The absorption peak at 3427.51 cm^{-1}, 3444.87 cm^{-1}, 3448.72 cm^{-1}, and 3427.51 cm^{-1} for each sample without swelling and sonication treatment, with swelling and sonication treatment, with swelling treatment and with sonication treatment could be assigned to -OH, but when compared to OH absorption peaks in the composite spectrum is weaker than the absorption peaks in the pure cellulose spectrum. The spectrum showed the presence of N-H stretching vibration of composite compounds at 3226.91 cm^{-1}, 3228.84 cm^{-1}, 3228.84 cm^{-1} and 3211.48 cm^{-1} [13].

The absorption peaks at 1568.13 cm^{-1}, 1570.06 cm^{-1}, 1568.13 cm^{-1} and 1566.20 cm^{-1} was assigned as vibration of the N-H. The bands at 1487.12 cm^{-1}, 1487.12 cm^{-1}, 1485.19 cm^{-1} and 1483.26 cm^{-1} can be assigned to stretch vibrations of C=C [14]. The bands at 1303.03 cm^{-1}, 1301.95 cm^{-1}, 1303.88 cm^{-1} and 1303.88 cm^{-1} could be assigned to C-N stretching vibration [15]. Strong peaks at 1149.57 cm^{-1}, 1147.65 cm^{-1}, 1149.57 cm^{-1} and 1145.72 cm^{-1} correspond to vibrations of the C-N quinoid ring. The bands of C-H on a 1,4 disubstituted benzene at 817.82 cm^{-1}, 815.89 cm^{-1}, 817.82 cm^{-1} and 815.89 cm^{-1} is also well known in the spectrum of the dispersed fibers [16].

Value of PANI-Cellulose Conductivity

Conductivity measurement of PANI-Cellulose composite was carried out using LCR-Meter. Measurement results are shown in Table 1.

Table 1. PANI-Cellulose Composite Conductivity Value

Ratio comparison of cellulose and aniline	Value of PANI-Cellulose Conductivity without Swelling and Sonication (S/cm)	Value of PANI-Cellulose Conductivity Swelling and Sonication (S/cm)	Value of PANI-Cellulose Conductivity Swelling (S/cm)	Value of PANI-Cellulose Conductivity Sonication (S/cm)
1:1	$2.78x10^{-7}$	$1.44x10^{-6}$	$3.12x10^{-6}$	$2.82x10^{-6}$
1:5	$3.97x10^{-4}$	$9.01x10^{-4}$	$9.69x10^{-5}$	$1.53x10^{-6}$
1:10	$2.49x10^{-4}$	$1.07x10^{-4}$	$1.52x10^{-4}$	$2.31x10^{-3}$
1:15	$5.04x10^{-4}$	$3.27x10^{-4}$	$9.59x10^{-5}$	$3.12x10^{-3}$
1:20	$2.32x10^{-4}$	$8.54x10^{-5}$	$5.86x10^{-5}$	$2.25x10^{-3}$

The conductivity values of PANI-Cellulose composites without swelling and sonication increased with the increase in a weight ratio of Aniline/Cellulose. The increase of aniline added in the polymerization process will increase conductivity which due to by monomers which available for the protonation process by the dopant HCl. The increase monomer is available for the protonation process will be formed longer polymer to [17].

The decrease in conductivity values that occur in the addition of considerable aniline due to an incompletely protonated aniline monomer or unprotonated nitrogen atom in PANI [18].

The difference treatment showed that by sonication method to PANI-Cellulose composites in swelling sonication methods could increase the conductivity value. The PANI-Cellulose conductivity swelling sonication methods value at the optimum was found in the 1: 5 Cellulose/Aniline weight ratio. According to [1], cellulose acidified with sonication will make the acid penetrate all parts of the cellulose so the added aniline will interact better. In contrast to PANI-Cellulose composites without swelling and sonication, aniline does not penetrate to every part of cellulose so that its presence is only some parts of acidified cellulose.

Based on the conductivity values shown in Table 1, the conductivity values for composites swelling method showed lower values than other treatments. This is due to the presence of DMSO which can interfere with the protonation process so the amount of polyaniline that undergoes a doping process becomes less [2]. The mechanism of disruption of the polyaniline protonation process by DMSO is shown in Figure 6.

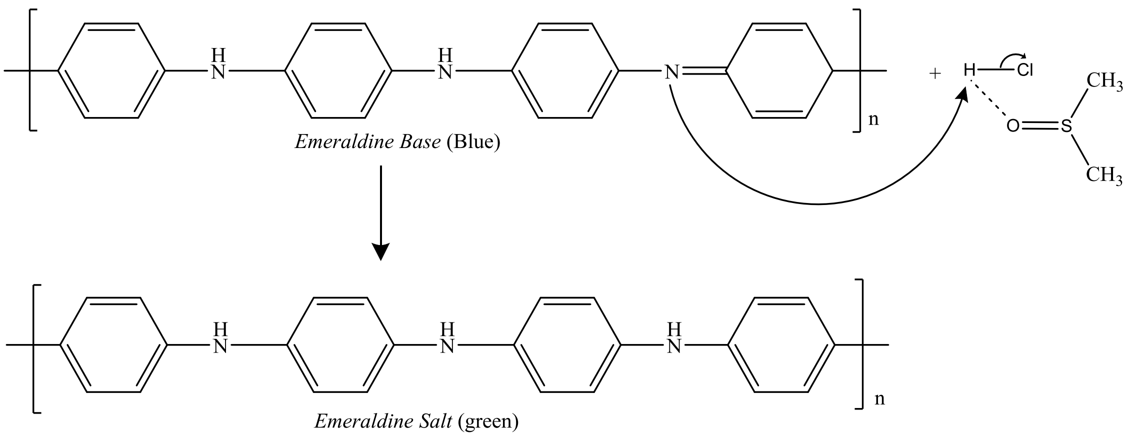

Figure 6. Mechanism of disruption of the polyaniline protonation process by DMSO [19]

Sonication method can influence the conductivity value of PANI-Cellulose composite. In Table 1, PANI-Cellulose composites sonication method yielded a conductivity value of 0.00312 S/cm at the optimum value of an cellulose/aniline ratio is 1:15. In this treatment, it can be seen that the increase of aniline concentration is proportional to the conductivity value in the sample. The considerable of aniline added, will be formed polyaniline too much then will increase the conductivity of the polymer. The decrease in conductivity values also occurs in samples with the addition of aniline considerable to the sample without swelling and sonication treatment. Ultrasonic is used as homogenizers to increase the similarity in form and stability [20]. Cavitation effects in liquid chemical reactions will increase speed, more efficient energy, improved performance of phase transfer catalysts, metal/solid activation and increased reactivity of reagents or catalysts [21]. With the result that the sonication process can increase the reactivity of HCl to form ions (H^+).

From Table 1 it can be seen that there are differences in the conductivity values produced by each sample with different treatments. Conductivity value at the optimum conditions of PANI-Cellulose composite without swelling and sonication was 5.04×10^{-4} S/cm, PANI-Cellulose swelling and sonication method composite was 9.01×10^{-4} S/cm, PANI-Cellulose swelling method composite was 1.52×10^{-4} S/cm and PANI-Cellulose sonication method composite was 3.12×10^{-3} S/cm. The difference in conductivity values is caused by differences in the synthesis method of PANI-Cellulose composites.

Morphology and Composition of PANI-Cellulose

The morphology and composition of PANI-Cellulose composites were analyzed using SEM-EDX.

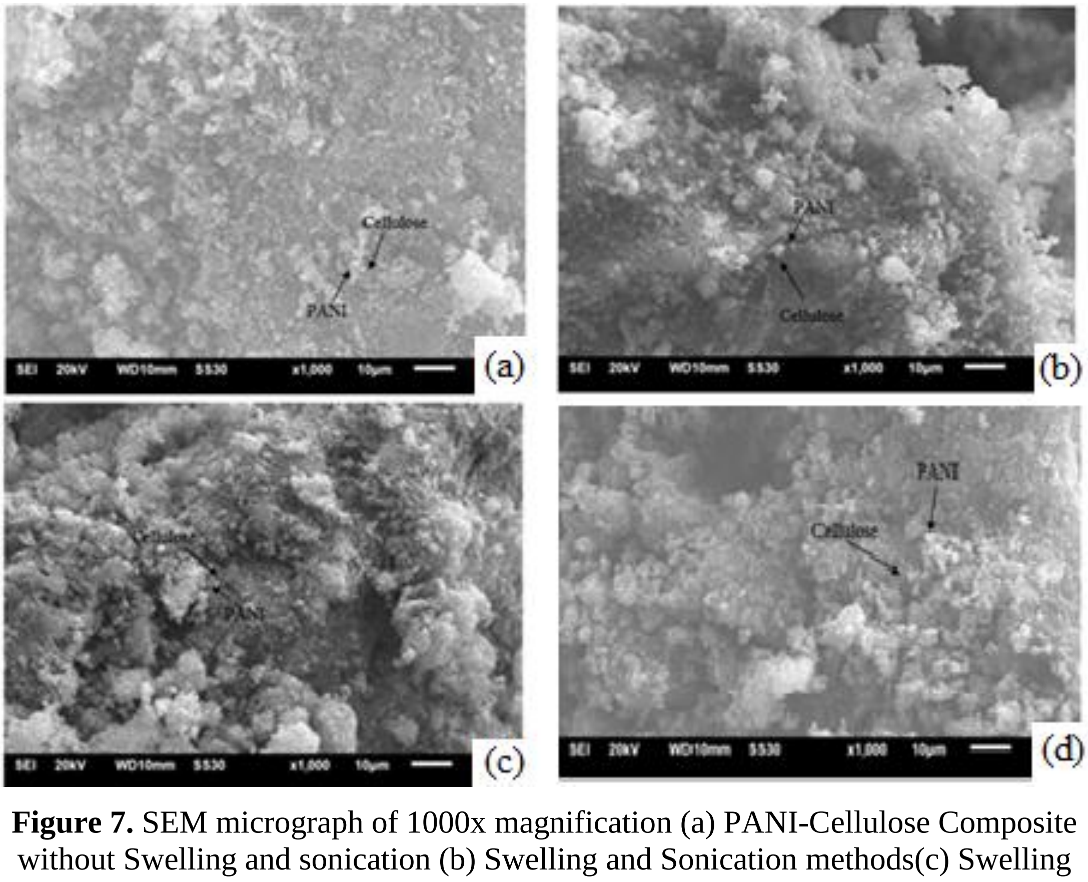

Figure 7. SEM micrograph of 1000x magnification (a) PANI-Cellulose Composite without Swelling and sonication (b) Swelling and Sonication methods(c) Swelling method (d) Sonication method

The results of the PANI-Cellulose composite characterization by SEM showed the cellulose surface covered by polyaniline in the granular form [3]. According to [2], the swelling process carried out on cellulose allows aniline to cellulose fibers. So that it can be seen in Figure 7 (b) and (c) that aniline is dispersed between the cellulose structures that look swollen after going through the swelling process. PANI-Cellulose composites without swelling and sonication method (Figure 7 (a)) showed PANI dispersed on the cellulose surface but less compared to PANI composites with sonication method (Figure 7 (d)). The sonication method specimens, PANI which covers the cellulose will increase compared without the sonication method.

SEM micrograph of PANI-Cellulose composite showed that the synthesis results of composites had the aggregate structure in accordance with those reported by [22]. Aggregates are formed due to stirring factors which are not constant speed and the influence of the drying process. High stirring speeds due to polyaniline to break and form aggregate. In the drying process, the water molecules are released constantly, causing adjacent molecules to form large aggregates [23]. In addition to the results of SEM, EDX results are also obtained in the form of percentage content of elements contained in the composite.

Table 2. Composite Composition of PANI-Cellulose ratio (cellulose: aniline) 1:15

Element	Wt %			
	PANI-Cellulose Composite without Swelling and sonication	PANI-Cellulose Composite Swelling and sonication	PANI-Cellulose Composite Swelling	PANI-Cellulose Composite sonication
Carbon (C)	38.32	41.10	44.31	41.48
Nitrogen (N)	24.44	39.24	24.12	43.48
Oxygen (O)	2.15	4.20	2.59	2.20
Chlorine (Cl)	13.28	6.12	13.87	7.84
Potassium (K)	0.94	0.46	0.45	0.53
Chrome (Cr)	2.77	0.80	1.94	1.06
Aurum (Au)	18.11	8.08	12.72	3.41

Table 2 shows the element composition contained in PANI-Cellulose composites including Carbon, Oxygen, Nitrogen, Chlorine, Potassium, Chromium and Gold. Carbon and Oxygen are cellulose constituent hydrocarbons, element N is the constituent element of PANI. The chlorine element is an anion produced by PANI by HCl. Based on the results obtained it can be seen that there are still impurities in the composite with elements such as K and Cr. This is because washing PANI-Cellulose composites using HCl and acetone is not done perfectly. According to [24] impurities in the form of residual oxidants can be lost when washing PANI-cellulose with HCl and acetone.

Electricity of PANI-Cellulose

The results of the PANI-Cellulose composite electrical test results are presented in Table 3.

Table 3. PANI-Cellulose composite electrical value

Treatments	Voltage (V)			Electric Current (mA)		
	Cellulose:Aniline Ratio			Cellulose:Aniline Ratio		
	1:5	1:10	1:15	1:5	1:10	1:15
Without swelling and sonication	1.20	1.08	1.30	23.7	22.0	7.3
Swelling and sonication	1.30	1.27	1.42	58.4	36.9	35.0
Swelling	1.15	1.20	1.29	7.1	11.8	15.2
Sonication	1.28	1.29	1.31	30.4	36.9	71.4

Increased conductivity values will due to an electric current to increase. For certain materials such as semiconductors, the voltage is inversely proportional to the electric current [25]. Table 3 shows the differences in the electrical quantities produced by PANI-Cellulose composites. PANI-Cellulose composite without swelling and sonication method at optimum conditions produced a voltage of 1.30 volts and a current of 7.3 mA. PANI-Cellulose composite with swelling and sonication methods produces the highest voltage of 1.42 volts and a current of 35.0 mA. PANI-Cellulose swelling method composite produces a voltage of 1.29 volts and a current of 15.2 mA. PANI-Cellulose sonication method produces greater conductivity values than PANI-Cellulose Composites with other pretreatments. This causes the generated electric current to be greater than the other samples which are 71.4 mA with a voltage of 1.31 volts.

CONCLUSION

Synthesis of Polyaniline-Cellulose composites from corn cobs as solid electrolytes in batteries with sonication method can produce higher conductivity values compared to composites with another method. The optimum conductivity value of PANI-Cellulose sonication method is 0.00312 S / cm, the resulting voltage is 1.31 volts at a current of 71.4 mA.

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