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RESEARCH ARTICLE

DOPANT, IMMERSION TIME EFFECT, AND HYDROLYSIS ONTO POLYANILINE/BACTERIAL-COMPOSITES: CONDUCTIVITY STUDIES

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Abstract

The composite of conductive polyaniline was synthesized using the in situ chemical polymerization methods on cellulose to form PANI-cellulose composites. Polyaniline can be composited with a cellulose matrix (nata de coco) due to its abundance, low price, and environmental friendliness. Ammonium peroxodisulfate (APS) was usedas an initiator for the oxidative polymerization of aniline. Characterization of PANI-Cellulose Bacterial composite was drawnusing FT-IR and SEM, while the conductivity and electric quantities both using LCR-meter, FT-IR spectra, and SEM The PANI-cellulose bacterial composite with the various concentration dopant of H_2SO_4 methods has the highest conductivity than PANI-cellulose bacterial composite with the dopant of HCl methods.

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Introduction:

Polyaniline has the advantages of being easy to synthesize, stable in the environment, and resistant to corrosion (Hu et al., 2011). However, polyaniline is a conductive polymer with a lower conductivity than other conductive polymers such as polypyrrole, poly(3-hexylthiopene, poly(3-alkyleterthiopene), polyparaphenylene, etc. (Rahman et al., 2008). that the cellulose-polyaniline composite model can be explained because of the hydrogen bonding between the hydroxyl groups of cellulose (nata de coco) and polyaniline, as shown in Figure 1 below:

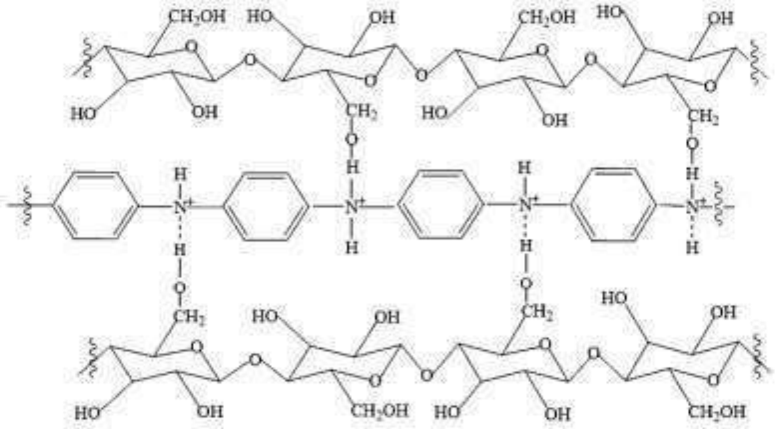

Figure 1:- Polyaniline-BC dopant HCl conductive composite models.

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The conductivity of polyaniline ranges from 1-100 S/cm, which is relatively low compared to the conductivity of other conductive polymers (Bhadra et al., 2009). Increasing the conductivity of polyaniline can be done by adding dopant compounds by reducing the electron density in the polyaniline chain so that polyaniline with a high electron distribution is obtained. Dopants are additional compounds used to increase the conductivity of conductive polymers, one of which is polyaniline. Generally, the dopant compounds used are strong acids that can donate or donate protons. Some dopant compounds that are often used in the polymerization of polyaniline are hydrochloric acid, sulfuric acid, phosphoric acid, and several types of metals (Jarad et al., 2016). Bacterial cellulose is cellulose formed from the secretion of the bacterium Acetobacter xylinum. Bacterial cellulose has a high surface area and porosity (Chawla et al., 2009). In addition, cellulose can interact with polymers to form new bonds found in cellulose fibers to allow cellulose as a composite matrix with polyaniline (Wang et al., 2012). polyaniline using in situ polymerization synthesis. So that the current research will develop a study on the effect of cellulose thickness and dopant type on the conductivity of PANI/BC composites. The results of the synthesis were characterized by electrical properties using an LCR meter and electrical structural characteristics using FTIR (Fourier Transform Infra Red).

Experimental Section

Materials:

The equipment used includes beakers, Erlenmeyer glasses, measuring flasks, stirring rods, simple presses, dropper pipettes, Mohr pipettes, ball pipettes, desiccators, glass funnels, scissors, and automatic shakers. Characterization tools include an LCR meter as well as a set of Fourier Transmittance Infra-Red (FTIR) tools. The materials used include aniline p.a, nata de coco, chloroform p.a, ammonium Ammonium Peroxodisulfate (APS) p.a, distilled water, and sulfuric acid (H_2SO_4) pa, hydrochloric acid (HCl), acetone, Merck NaOH.

Purification of Bacterial Cellulose

Bacterial cellulose (BC) with incubation of 3 days and 11 days was prepared. BC soaked in running water for 24 hours. Then soaked in hot water at a temperature of 80-90 C for 2 hours. Furthermore, the BC was washed with 2% NaOH at a temperature of 80-90^{o}C for 2 hours and soaked again in hot water at a temperature of 80-90^{o}C Nata de Coco which has been purified is then cut to a size of -+ 3 cm × 4 cm (l×w).

Synthesis of PANI/BC Composite

Polymerization using the optimum concentration ratio carried out by Wang et al. (2012) with a molar ratio of Aniline: HCl or H_2SO_4 Ammonium peroxodisulfate (APS) is 1 M: 1.2 M: 1 M. Polymerization is carried out by anin situ process. BC with an incubation period of 3 and 11 days was added to a mixture of APS (15 mL) and dopant (15 mL) for 2, 4, and 6 hours, respectively. Nata de coco BC which had been diffused by APS and dopant (HCl and H_2SO_4) was then immersed in 25 mL of aniline for 30 minutes. Then it was pressed to a certain thickness and continued with drying at room temperature for 24 hours. The formed PANI/BC composite was washed with acetone to remove the remaining unreacted aniline and dopant.

Characterization of PANI-BC

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

Result And Discussion:

Synthesis of PANI/BC Composite

The method used is in situ oxidative polymerization, where the polymerization is carried out in stages from aniline monomers to obtain a Pani/BC composite. The BC immersion in a mixture of APS and HCl or H_2SO_4 did not show any color change. However, after soaking with aniline monomer, there was a color change to dark green, tending to black in all parts of BC. This color change indicates that aniline polymerization has taken place into polyaniline in the form of emeraldine salt. The resulting material obtained after polymerization was then dried at room temperature(+-27 C) for 24 hours to reduce the moisture content in the Pani/BC composite. The reaction mechanism of polyaniline polymerization by oxidation can be shown in Figure 2 below

Propose Mechanism Polymerization of Polyaniline Oxidative

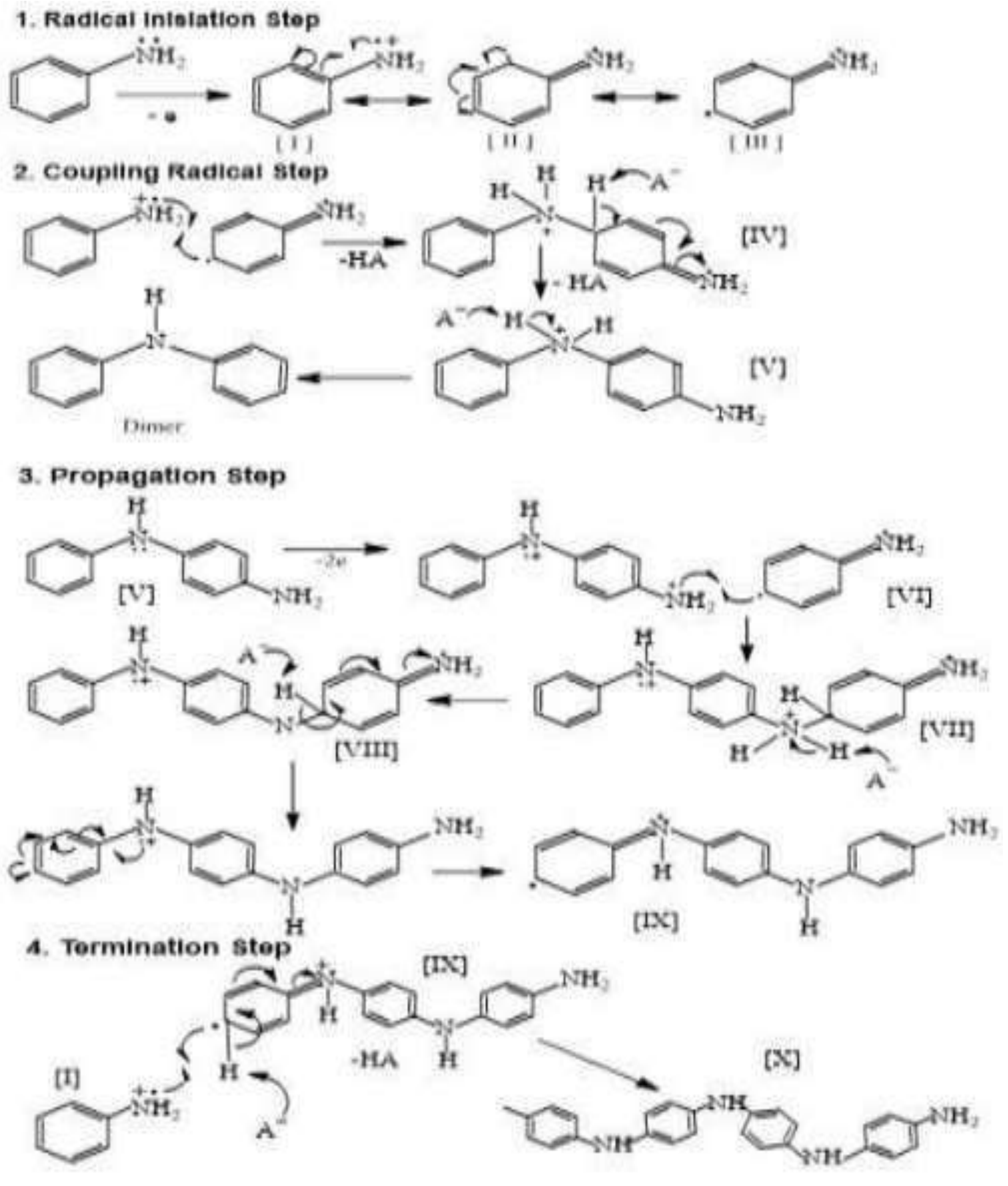


Figure 2:- Propose Mechanism Polymerization of Polyaniline Oxidative.

Comparison of Dopant Compounds

The role of dopant compounds greatly affects the increase in the conductive properties of polyaniline. One of the dopant factors that can act as a conductivity-enhancing compound is the ability to donate protons (H^+) to the polymer chain. The dopant used is HCl and H_2SO_4. The two dopants have different properties. In an HCl dopant, protonation can occur as much as once at the imine site in the polyaniline chain. Whereas in H_2SO_4 protonation can occur twice at the imine site. Shown in the image below.

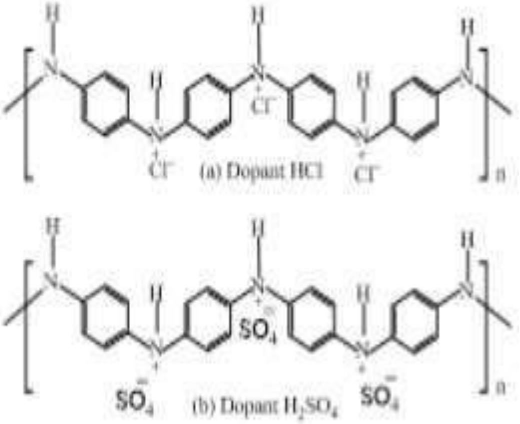


Figure 3:- Structure Polyaniline Emeraldine-Salt (a) Dopant of HCl; (b) Dopant of H_2SO_4

In Figure 3 it can be seen that the higher the positive charge, the higher the conductivity of the polyaniline. In H_2SO_4dopant it is possible to have a greater positive charge than HCl so that the conductivity of H_2SO_4 doped composite is higher than HCl. The conductivity of the HCl-doped PANi/BC composite was 6.36×10^{-6} S/cm, while the H_2SO_4doped composite had a conductivity of 2×10^{-3} S/cm. Based on table 2 mentioned above, it can be illustrated the structure of polyaniline in each dopant.

Analysis of FTIR spectra (Fourier Transform Infra Red) of composites

FTIR analysis was used to study and observe the effect of immersion time in the mixture of APS and HCl or H_2SO_4 for each functional group possessed by PANi. Before this step, it is necessary to analyze the changes in the absorption peaks contained in BC as a composite matrix, after the synthesis of the PANi/BC composite. Referring totable 1 contains data on the absorption peaks of each type of vibration and Figure 4 shows the IR spectra of BC and PANi without dopants. There was a change in the absorption peak at 3344 cm^{-1} belonging to BC which experienced a widening of the spectra to 3230 cm^{-1}. This indicates that there has been an interaction between the nitrogen atom in polyaniline and the hydroxyl group of BC, resulting in a widening of the absorption peak but with atransmittance that tends to be sloping. Changes also occurred with the appearance of typical polyaniline peaks at 1587 cm^{-1} and 1496 cm^{-1} which indicated the presence of quinoid and benzenoid groups. Meanwhile, the absorption peak is 1062 cm^{-1} which is ether as a glycoside bond in BC.

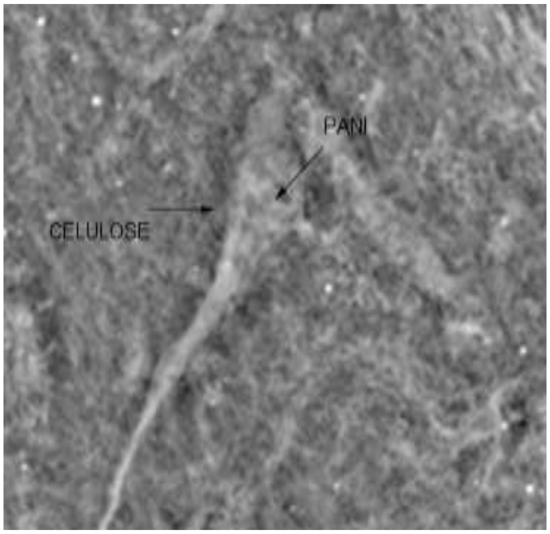


Figure 4:- Spectra SEM of PANi/BC Composite.

On the influence of the immersion time of the mixture of APS and HCl or H_2SO_4quantitative analysis is needed on the absorption peaks of quinoids and benzenoids. This is necessary to determine the effect of the structure formed due to immersion time, where the effect of quinoid and benzenoid composition affects the electrical properties of polyaniline (Hatchett, 1999). Figure 6 shows the IR spectra of the PANi/BC composite doped with HCl and H_2SO_4 with quinoid (~1500 cm^{-1}) and benzenoid (~1400 cm^{-1}) moieties. Through quantitative analysis of absorbance, data on the composition of quinoid and benzenoid on the conductivity produced by each immersion were obtained

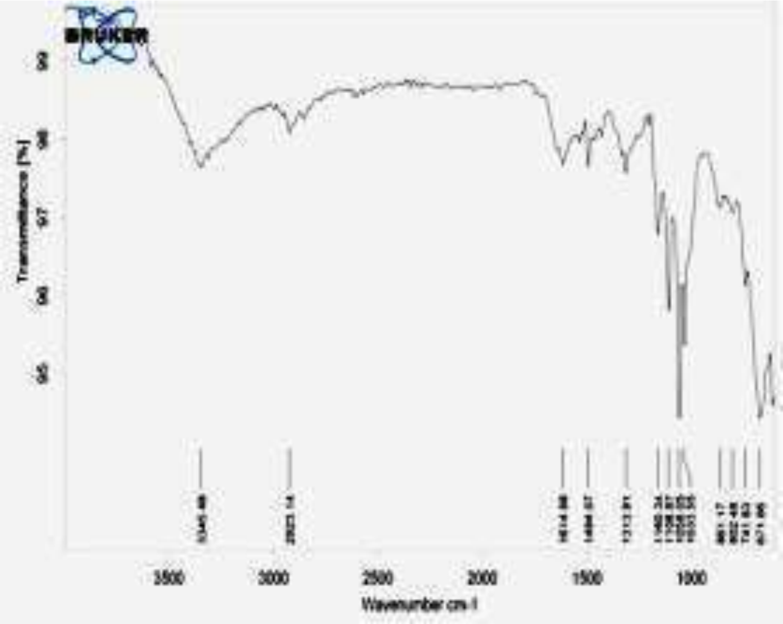


Figure 5:- FTIR Spectra of PANi/BC Composites.

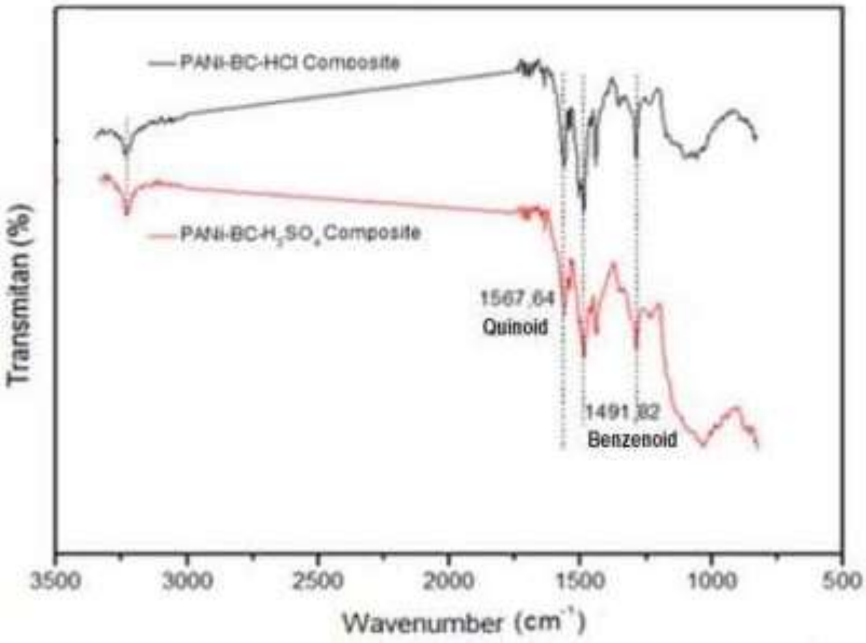


Figure 6:- FTIR spectra of polyaniline and PANi-BC composites.

The results of the FTIR spectrum of polyaniline have the following peaks: 3228.31 cm^{-1}; 1539.06 cm^{-1}; 1426.18 cm^{-1}; 1297.28 cm^{-1}; 1154.84 cm^{-1};1019.53 cm^{-1}; ; and 874.39 cm^{-1}; while the bacterial polyaniline-cellulosic composite with a concentration of 3.5M HCl resulted in the FTIR spectrum at Figures 5, and 6 showing peaks at 3401.12 cm^{-1}; 3230.39 cm^{-1}; 1637.70 cm^{-1}; 1565.92 cm^{-1}; 1491.14 cm^{-1}; 1442.95 cm^{-1}; 1288.79 cm^{-1}; 1187.11 cm^{-1}; 1050.92 cm^{-1}; and 739.83 cm^{-1}; The composite FTIR spectrum contained a peak of 3401.12 cm^{-1}; as a stretch of O-H anda peak of 3230.39 cm^{-1}; as a type of bonding of N-H. The O-H stretching peak is the identity of the bacterial cellulose present in the composite and the N-H peak is evidence of polyaniline inclusion in the composite matrix. The results of the spectrum of polyaniline and polyaniline-cellulose composites of bacteria in the study can be seen in Figure 6. The FTIR spectra of the PANi/BC composite doped with H_2SO_4 and HCl (Figure 7), show two peaks of a quinoidring and a benzenoid ring. At the same oxidation state (emeraldine base), the quinoid and benzenoid rings are cross-linked. These two parts are the main constituents of polyaniline which play an important role in its electrical properties. However, the addition of H_2SO_4 and HCl dopant will affect the composition of the benzenoid ring in polyaniline. According to the reaction mechanism of the dopant with polyaniline, the imine site (-N=) in the quinoid. The ring allows the protonation of strong acids to occur. The protonation of a strong acid at the imine site results in a changein the quinoid ring to benzenoid. The change of quinoid to benzenoid is accompanied by changes in the electrical properties of polyaniline which are increasing. The greater the composition of benzenoid in the polymer chain, the greater the conductivity. However, not the overall reaction between the dopant and the imine site in the quinoid will form benzenoid. This is influenced by the acid concentration, the strength of the acid initiation, and the ability of the acid to protonate the imine site. A(quinoid) /A(benzenoid) where A(quinoid) always has a higher value ratio than A(benzenoid)

Table 1:- FTIR Analysis of Composite PANi-BC.

Vibration	Wave number (cm^{-1})				
	BC	Composite Dopant HCl	Composite Dopant H_2SO_4	Pure of PANi	Composite of PANi-BC
-NH amine	-	3230,18	3232,19	3200,86	-
-OH stretching	3344	-	-	-	-
C-H sp^2	2888	-	-	2926,44	-
C=N quinoid	-	1563,71	1563,71	1587,56	1557
C-N benzenoid	-	1491,82	1489,35	1496,63	1483
C-O-C ether	1062	-	-	-	-

Increasing the concentration of dopants in the polymerization will increase the degree of conductivity caused by the increase in protons (H^+) by the filled HCl dopant to the emeraldine slat structure. The increase in the conductivity value can be seen in Figure 7.

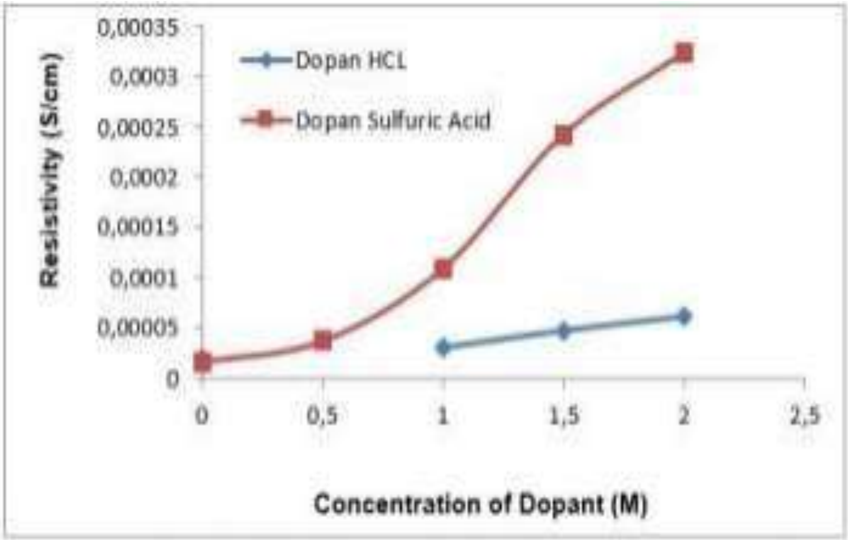
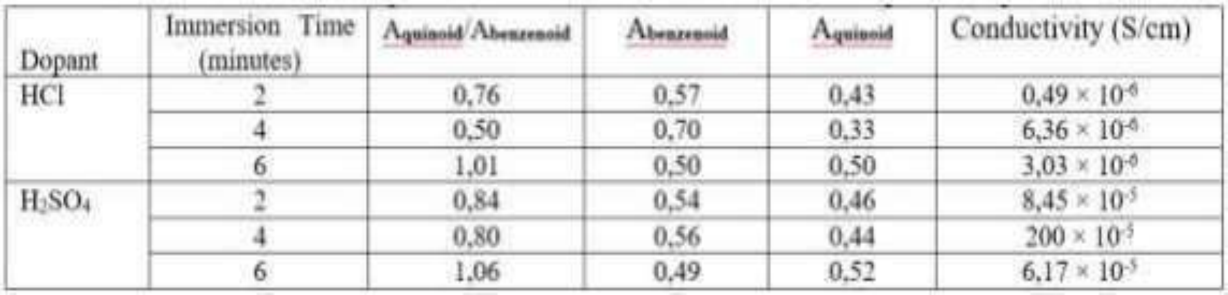


Figure 7:- The conductivity of PANi-BC/HCl and PANi-BC/H_2SO_4 composites.

Table 2:- Effect of Immersion of Dopants HCl and H_2SO_4 based on PANI-BC composites Aquinoid / Abenzenoid).



Dopant	Immersion Time (minutes)	$A_{quinoid}/A_{benzenoid}$	$A_{benzenoid}$	$A_{quinoid}$	Conductivity (S/cm)
HCl	2	0,76	0,57	0,43	$0,49 \times 10^{-6}$
	4	0,50	0,70	0,33	$6,36 \times 10^{-6}$
	6	1,01	0,50	0,50	$3,03 \times 10^{-6}$
H_2SO_4	2	0,84	0,54	0,46	$8,45 \times 10^{-5}$
	4	0,80	0,56	0,44	200×10^{-5}
	6	1.06	0,49	0,52	$6,17 \times 10^{-5}$

Based on table 2, it has been shown that the immersion time of BC in a certain solution has a sufficiently large water absorption ability against a thin film, thus enabling a thermodynamic equilibrium in the BC. The longer the immersion time of BC in a solution using a room temperature of 25-27°C, the more water content is substituted by APS and dopants. In this study, BC was immersed in a mixture of APS and H_2SO_4 to replace the presence of water content in the BC. However, the polyaniline formed from the polymerization of aniline was also affected by the amount of APS that had been absorbed into the BC. The density of polyaniline in BC can also affect the magnitude of the resistance and conductivity. Highest conductivity with an immersion time of 4 hours. If it is related to the composition of benzenoid and quinoids (HCl-dopant composites), the benzenoid is 0.67 and the quinoids are 0.33. Meanwhile , the H2SO4 benzenoid dopant was 0.56 and the quinoid was 0.44. The effect of benzenoid composition on the high conductivity of PANi is because the benzenoid part allows the formation of radical cations on the nitrogen atom so that the more formed the electron mobility in the PANi chain will be better. The results of research conducted by Yusningsih, et al 2017 the conductivity properties of conductive material are influenced by the polymer arrangement formed, with a more compact arrangement allowing the resulting resistance to be smaller. In the sample with 10 days BC incubation time at table 2, there was a significant decrease in conductivity at 4 and 6 hours BC immersion time, 2.00 × 10-3 S/cm and 6.17 × 10-5 S/cm, respectively. . This phenomenon could be caused by the volume of absorbed APS and H_2SO_4more than the 5-day BC incubation so that the polyaniline bound to the –OH group had a large number of crowded arrangements. The influence of the small conductivity value can be caused by the poor density of the polymer formed, causing electrons to be trapped in the localized state, and in some parts, there is no charge conduction. Yuningsih et al.2017 have low conductivity values of 0.49 × 10-6 S/cm and 8.45 × 10-5, respectively. This is because the APS that is diffused into the BC is not optimal, so a little polyaniline is formed. Meanwhile, at 4 hours of immersion in Table 2, the highest conductivity for each use of HCl and H_2SO_4dopant was 6.36 × 10-6 S/cm and 200 × 10-5 S/cm, respectively. immersion time of 4hours indicated the optimal time for BC to diffuse the oxidizer so that more polyaniline was synthesized. However, at 6 hours of immersion in Table 2, the conductivity values decreased significantly. According to research conductedby Yuningsih et al 2017 and yuningsih, et al, 2018 that when using aciddoping with a concentration of 4 M, the conductivity decreased and a polyaniline hydrolysis reaction occurred becausethe system has a water absorption ability of 99% of the thin film, thus allowing a thermodynamic equilibrium to occurin BC. The longer the immersion time of BC in a solution using room temperature of 25-27°C, the more water contentis substituted by APS and dopants. In this study, BC was immersed in a mixture of APS and $H_2SO_4$for 6 hours to replace the presenceof water content in BC and HCl or $H_2SO_4$and a hydrolysis reaction could occur by strong acids against polyaniline into smaller molecules, namely p-aminoaniline and keto-aniline. as a product of hydrolysis.This shows that the greater the benzenoid composition in the PANi chain with a certain limit, the higher the conductivity will be. However, if the quinoid composition predominates in the PANi chain to a certain extent, a lower conductivityis obtained. The phenomenon in the table may be due to hydrolysis in the presence of strong acids such as HCL and H_2SO_4 as shown in Figure 8. below:

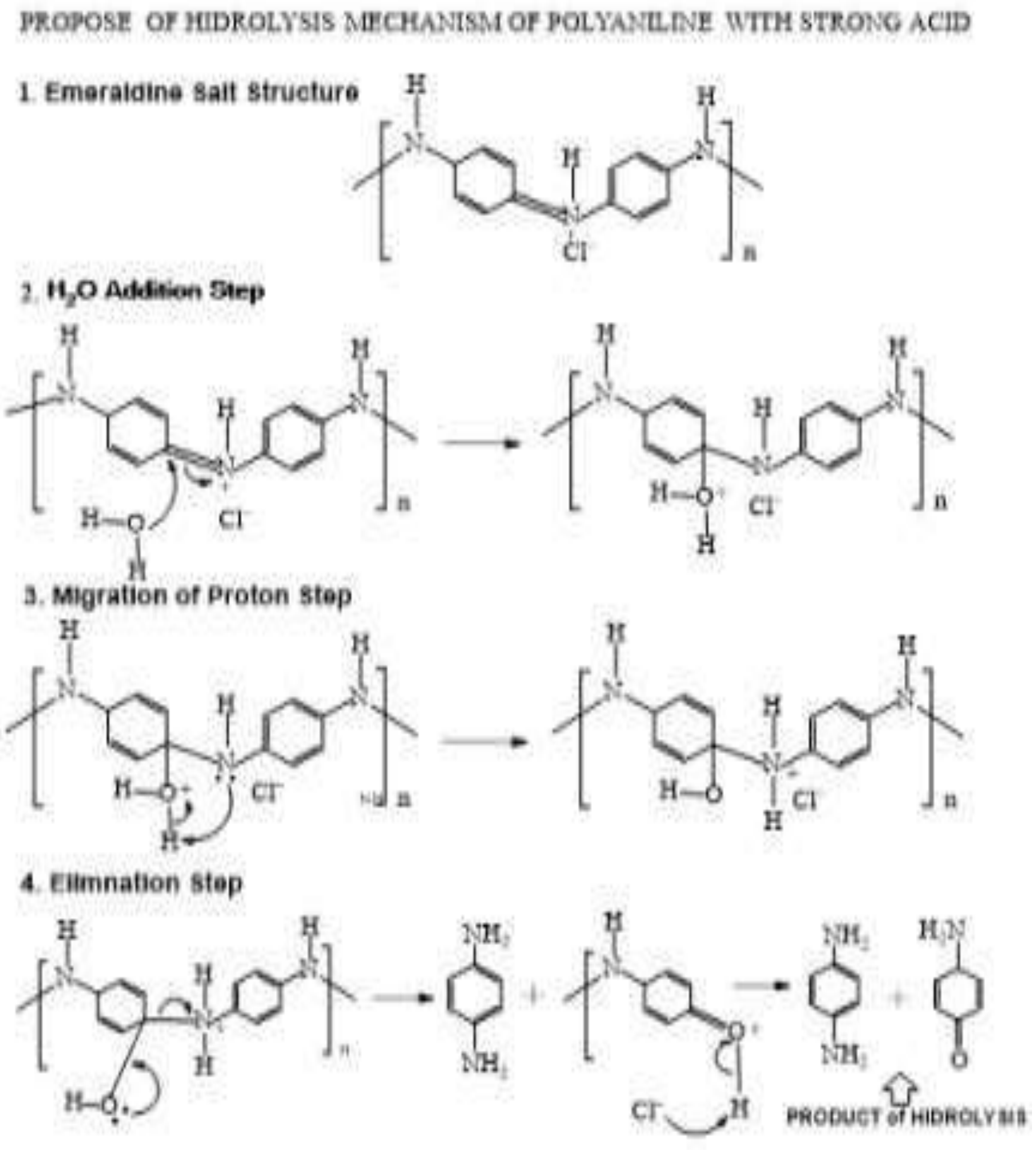


Figure 8: Propose Mechanism of Hydrolysis PANI by HCl.

Table 3: Effect of Concentration of Dopant HCl based on Conductivity Value of Polyaniline-BC Composites.

Treatment	Concentration of HCl (M)					
	0	1	1,5	2	2,5	3,0
Resistivity value (Ohm)	139	811	533	456	330	255
	131	841	555	414	358	258
	131	868	586	439	360	236
Conductivity value (S/cm)x10^{-5}	1,9	3,29	5,00	5,85	8,08	10,50
	1,9	3,17	4,80	6,44	7,45	10,30
	2,0	3,07	4,71	6,07	7,41	11,30
	2,0	3,07	4,71	6,07	7,41	11,30
Average Conductivity value (S/cm)x10^{-5}	1,95	3,17	4,84	6,12	7,63	10,7

Table 4:- Effect of Concentration of Dopant H_2SO_4 based on Conductivity Value of Polyaniline-BC Composites.

Treatment	Concentration of H_2SO_4				
	0 M	0,5 M	1 M	1,5 M	2 M
Conductivity value (S/cm)x10^{-5}	1,54	3,70	10,90	24,20	32,30

The highest conductivity value in this study was at 2M doping of $3.23x10^{-4}$ S/cm in Table 4 because with the addition of acid, concentration resulted in the emergence of free radical cations due to the oxidation polymerization reaction. This radical cation causes the double-bonded polyaniline to form an energy level between the valence bands. This causes the presence of free electrons which are charge carriers so the addition of the acid concentration will cause more free electrons to be bound to the polyaniline and cause the conductivity to increase. The results of this characterization are the results of the oxidation polymerization process on aniline monomer which produces polyaniline doped with H_2SO_4as a proton source, resulting in a change in its structure from Emeraldine Base to Emeraldine Salt which is conductive. Synthesis of polyaniline-cellulosic composite (nata de coco) obtained emeraldine salt and along with an increasing concentration of dopant H_2SO_4(0; 0.5; 1; 1.5; 2)M the conductivity value was higher. Judging from the range of conductivity values, polyaniline-cellulose (nata de coco) is a conductor

Conclusion:

Synthesis of Polyaniline-Cellulose composites from Nata de coco with dopant H_2SO_4 and HCl. Produce higher conductivity value composites with the dopant H_2SO_4l method higher than composites with the dopant HCl method. The optimum conductivity value of PANI-Cellulose dopant H_2SO_4is32, 30 x 10^{-5} S/cm .and HCl.is6,12x 10^{-5} S/cm.

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