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Polyaniline Emeraldine Salt Synthesis and Characterization: Effect of Aniline/Oxidant Molar Ratio and Acid Dopant Type and Concentration

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Abstract

Polyaniline (PANI) is considered one of the essential polymers due to its conductivity, affordable price, and high degree of stability, so it is successfully applied in several vital and strategic sectors, e.g., sensors, solar cells, fuel cells, and membranes. Polyaniline was synthesized by chemical polymerization using aniline monomer, ammonium peroxydisulfate (APS) as an oxidant and different mono, di, and tri-protonic acids, such as HCl, H_2SO_4, and H_3PO_4, respectively, as dopants. Each dopant was added using different concentrations from 0.5 to 2 M. The effect of dopant concentration on both polymer productivity and conductivity was investigated. X-Ray diffraction analysis (XRD) and Fourier-transform infrared spectroscopy (FTIR) were used to confirm the formation of PANI in the form of conductive emeraldine salt. The electrical conductivity of the synthesized polymer was also measured using a broadband dielectric spectrometer. The results revealed that the productivity and conductivity of PANI varied using different types of acids. The highest conductivities, 36.20, 74.80, and 49.30 mS/cm, were detected at concentrations 1.5 M HCl, 0.5 M H_2SO_4, and 2 M H_3PO_4, respectively. Empirical correlations were established using regression analysis to relate the oxidant-to-aniline (O/AN) molar ratio and acid concentration effects on PANI conductivity and productivity, demonstrating considerable effectiveness.

Keywords: Polyaniline, conductive polymer, chemical polymerization, productivity, characterization

1. Introduction

PANI polymer is considered one of the most popular conducting polymers used in many industrial applications such as sensors, photovoltaic cells, gas separation membranes, and metal protection from corrosion [1]. PANI polymer chain structure is made up of "head-to-tail" connected para-substituted monomer units.The chain structure formation and supramolecular structure in the polymer are important characteristics for the presence of a poly conjugated system and high conductivity of the polymer [2] . The polymer chain can create different structures. The first structure is one-dimensional structure in the form of nanofibers, nanorods, and nanotubes. The second structure is called planer, a two-dimensional structure like ribbons, nanobelts and nanoplates. The third one is three-dimensional particles in the form of microspheres and granules. These types of structures could act as the foundation of a more complex formation's structure. PANI has the ability to form these different structures [3–7]. The general chemical structure of the polyaniline is shown in Fig. 1. PANI structure consists of reduced (x) and oxidized (1 − x) blocks (0 ≤ x ≤ 1), and its chain consists of p-coupled aniline units. PANI conductivity can be improved by lengthening the polymer's conjugation chains and crystallinity [8].

PANI can exist in three different oxidation forms during the polymerization of aniline monomer due to the combination of benzenoid and quinoid rings. The first form is leucoemeraldine base when a fully reduced form occurred (yellow and x = 1), which contains only benzenoid rings. The second one is emeraldine, which occurs when a half-oxidized form occurs (dark green or blue and x = 0.5). The emeraldine forms are emeraldine salt (dark green) and emeraldine base (blue), depending on the acidic and basic conditions. The third form is pernigraniline when fully oxidized (purple and x = 0), which contains benzenoid and quinonoid rings as repeating units [9,10]. The emeraldine salt is the only conductive form of polyaniline. By doping or protonating the

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emeraldine base, the emeraldine salt can be produced. In the forms of polyaniline can be obtained using chemical oxidative or electrochemical polymerization reactions. The electrically conductive emeraldine salt has charge carrier mobility that varies from 10^{-3} to 10^{-1} cm2 $V^{-1}s^{-1}$ and a conductivity of $10^{-2} - 10^{0}$ S/cm [11,12].

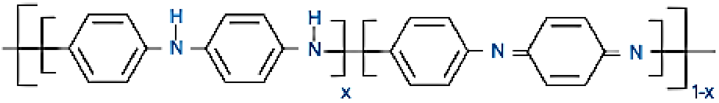


Fig. 1: Polyaniline chemical structure.

By using oxidants or suitable potential for polymerization of aniline in acidic medium, green conductive emeraldine salt is produced. Emeraldine salt is easily converted to dark blue pernigraniline salt through oxidation, or it can become violet pernigraniline base through interaction with alkali. Emeraldine salt can also be reduced to produce a transparent leucoemeraldine base or changed into blue emeraldine base in a reaction with alkali. The conductivity of conductive emeraldine salt decreases with both reduction and oxidation. PANI has a high degree of thermal stability, nontoxic material, and is stable in harsh chemical conditions. These characteristics make it easier to use it in different application like tissue engineering, medicine,membrane and biosensing [13–21].

The conductivity of PANI varied depending on several factors during the polymerization process. Processing conditions: aniline to oxidant ratio, temperature, time of polymerization, dopant acid type, dopant concentration, and washing. The ratio of aniline to oxidant plays a crucial role in determining the conductivity of PANI. A higher aniline-to-oxidant ratio can lead to a more ordered structure and higher conductivity. Different oxidants were used in the polymerization of aniline, such as ammonium persulfate, sodium vanadate, cerium sulfate, hydrogen peroxide, potassium iodate, and potassium dichromate [22]. Among these oxidants, ammonium persulfate is the most used. Ammonium persulfate is commonly used to dissolve aniline, initiate the polymerization process, and prevent the production of undesirable byproducts [23].

The application of low temperature in chemical polymerization offers the benefit of achieving fine particle size and a uniform size distribution of PANI, which suggests an increased surface area of the produced PANI and improve the electrical properties of PANI [24]. Moreover, the choice of dopant acid type and its concentration greatly affect the electrical properties, charge mobility, and stability of PANI. The higher the charge mobility, the higher the conductivity of PANI. This paper investigates the proper conditions to obtain conductive PANI using different acids and molar ratios of oxidant and aniline. In this work, different dopant types like HCl, H_2SO_4, and H_3PO_4 were used for the preparation of PANI. The prepared PANI was investigated to measure the conductivity and productivity in different conditions used.

2. Experimental

2.1. Chemicals

Aniline (AN) (99%, purchased from S D Fine-Chem Limited, India), Hydrochloric acid (HCl) (37%, purchased from EL-Nasr Pharmaceutical Chemicals Company, Sulfuric acid (H_2SO_4) (98%, purchased from Research Lab Fine Industries, India), Ortho-Phosphoric acid (H_3PO_4) (85%, obtained from Specialty Chemicals Seelze, GmbH). Ammonium peroxydisulfate (APS) (98%, obtained from Merck KGaA, Germany).

2.2. PANI synthesis

Polyaniline was synthesized using the oxidative chemical polymerization method. The first solution was prepared by adding aniline monomer to 50 ml acid solution with varied concentrations (0.5 to 2 M). The solution was sonicated for 30 min to ensure the good dispersion of aniline in the acid solution. Then, a second solution was prepared by adding different moles of oxidant APS and another 50 ml of the same acid. In an ice bath (4-5°C), drops of the second solution were added to the first sonicated solution under stirring for 1 h, and then kept for 24 h. in a temperature $\leq$ 5°C to ensure complete polymerization. A dark green precipitate indicated the formation of the conductive form of polyaniline (emeraldine salt). Then, the solution was filtrated, and the precipitate polymer separated and, washed several times with distilled water, and dried in a vacuum dryer at 70°C for 12 h. The obtained polymeric powder was compacted into pellets with a 10 mm diameter and 3 mm thickness to be tested.

To study the effect of oxidant APS on the PANI formation, different molar ratios of APS / aniline (0.5, 1, 1.25, 1.5, 2) and HCl (1M) as dopant were used. The study was extended to investigate the effect of different acids

HCl, H_2SO_4, and H_3PO_4 on PANI formation with various concentrations from 0.5 to 2M and a constant APS / aniline molar ratio 1.7. The flowchart in Fig. 2 shows the preparation procedures for PANI formation using different acids.

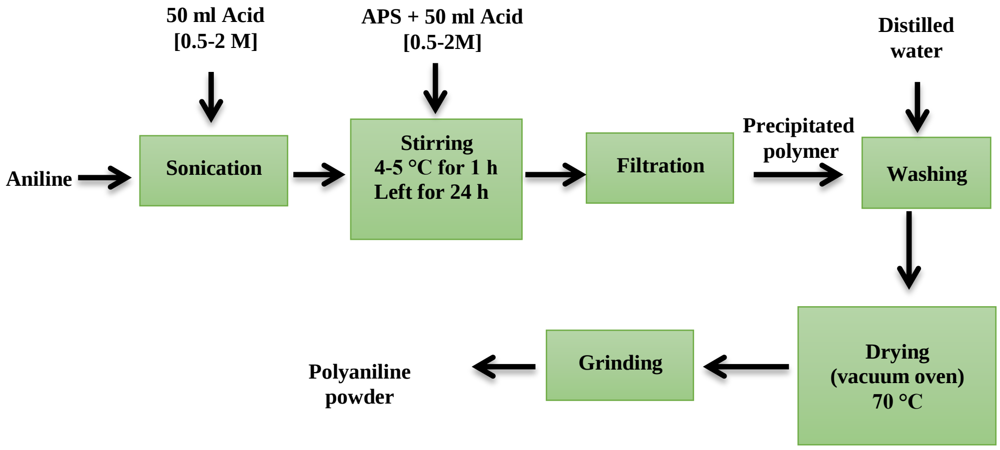


Fig. 2: Preparation of PANI flowchart.

2.3. Characterization

2.3.1. Fourier-transform infrared spectroscopy (FTIR)

The PANI samples were characterized using a Fourier Transform Infrared (FTIR) spectrometer (FT/IR-6100, JASCO, Japan), equipped a TGS detector and transimittance technique. The obtained FTIR spectra were recorded over a range of 400 to 4000 cm^{-1}. FTIR was used to identify the chemical bonds and groups obtained in each sample.

2.3.2. X-ray diffraction analysis (XRD)

XRD (EMPYREAN, DY 1007, Netherlands) was used to investigate the crystallinity of the prepared samples at 25°C measurement temperature using Cu anodic electrode material with 30 mA, 45 kV generator settings, and the position [°2 Theta] ranging from 4.0150 to 79.9610.

2.3.3. Energy dispersive X-ray analysis and Scanning Electron Microscope

Using the EDX device attached to SEM (JEOL JCM-6000 Neoscope). PANI samples were put under an X-ray spectrum using a probe with a high current of 15 V and high vacuum mode. SEM and EDX were used to investigate the structural appearance and the elemental analysis of each sample with different conditions.

2.3.4. Electrical conductivity measurement

The produced polyaniline was pressed into a pellet (11 mm diameter, 3 mm thickness) with a manual hydraulic press at 20 MPa. The electrical conductivity was investigated using broad-band dielectric Spectroscopy (BDS). The PANI-pressed discs were measured at ambient temperature and frequency range from 10^{-1} to 10^{-7} Hz using a Novocontrol Alpha analyzer.

2.3.5. Productivity (Yield %) of polyaniline

The yield of polyaniline produced was calculated using the equation below [18-19]:

$$Yield\ \% = \frac{mass\ of\ polyaniline\ produced}{mass\ of\ aniline\ monomer} \times 100$$

3. Results and Discussion

PANI was prepared using the chemical polymerization method, where monomer, oxidant (APS), and dopant (HCl, H_2SO_4 or H_3PO_4) were mixed in appropriate conditions. Some samples prepared using different dopants are shown in Fig. 3.

3.1. Effect of oxidant/aniline molar ratio on the productivity and conductivity

The preparation of polyaniline emeraldine salt requires the reaction of molecules of aniline and molecules of ammonium peroxydisulfate (APS) in an acidic medium. Thus, all the aniline in the reaction is consumed in the polymerization process to produce polyaniline. Fig. 4 shows the oxidation reaction. Mechanism between aniline and APS. The reaction produces sulfuric acid and ammonium sulfate (or ammonium hydrogen sulfate) as by-products [27,28]. Low pH is appropriate for the head-to-tail coupling of aniline monomers; hence, the process is conducted in a strongly acidic environment [29]. All Experiments were carried out at temperatures 4-5 °C to avoid any structural defects in PANI samples. According to [30,31], a low temperature is preferred for polymerization to produce defect-free PANI. Experiments showed that 20–24 h of polymerization were necessary to achieve optimal electrical conductivity.

The effect of molar ratio of oxidant/aniline (O/AN) shows an increase in productivity from 51.55 to 142.83% by increasing the molar ratio from 0.5 to 1.4. In contrast, the continuous increasing of molar ratio leads to decreasing productivity, as shown in Table-1 and Fig. 5. The maximum yield of polyaniline was observed at a 1.4 molar ratio. The yield reached 142.83% as all the aniline was consumed and oxidized to form polyaniline. A ratio of more than 1.4 may lead to over-oxidation that may cause part of the aniline to be converted to quinone, leading to a decrease of the yield. The high yield above 100% may be due to the participation of counter ions, like sulfate or hydrogen sulfate anions, during the protonation of PANI (reduction of APS) along with the chloride anions. This would lead to an apparent increase in the yield [32].

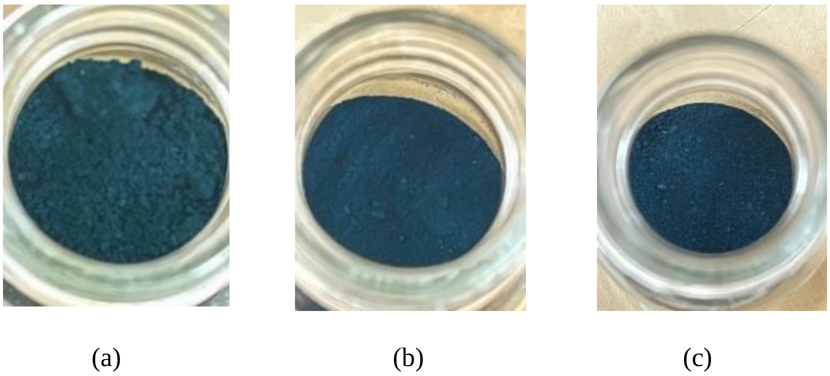


Fig. 3: Some samples prepared using different dopants (a) HCl, (b) H_2SO_4, and (c) H_3PO_4).

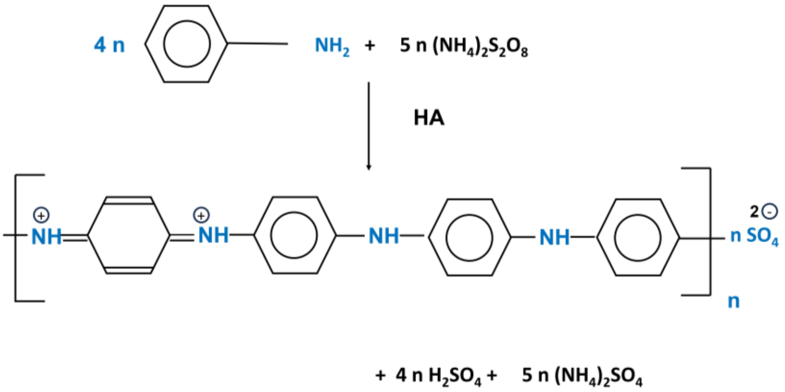


Fig. 4: The oxidation reaction of aniline and ammonium peroxydisulfate in acidic aqueous medium and the side reaction products (sulfuric acid and ammonium sulfate).

The Conductivity of PANI samples were compressed to disc form to measure the conductivity. The samples of molar ratio (O/AN from 0.5 to 2) were measured at varied frequencies from (10 to 10^7 Hz). Fig. 6 shows the plot between conductivity and log frequency for PANI samples. With increasing the Frequency, the conductivity of PANI samples shows stability until 10^5 Hz; then, an increase of conductivity was observed above 10^5 Hz. This indicates the presence of disordered materials due to polarons' contribution, which travel progressively shorter lengths along a polymer chain, so conductivity rises at high frequencies, as shown in Fig.6 [26-27].

Table 1: The effect of the oxidant/aniline molar ratio on the conductivity and yield of PANI.

O/AN	AN (ml)	Oxidant (APS) (g)	Acid Dopant (M)	Yield (g)	Conductivity (mS/cm)
0.5	4.558	5.704	HCl [1M]	2.4	8.75
1		11.409		4.5	6.09
1.25		14.26		5.95	10.81
1.4		15.972		6.65	18.99
1.7		19.395		5.98	23.14
2		22.818		4.96	5.11

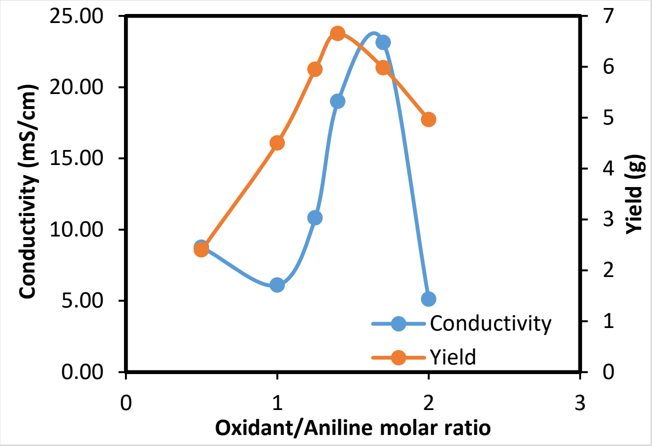


Fig. 5: The effect of O/AN molar ratio on PANI yield and conductivity (1M HCl).

Owing to the stability of material, the study of conductivity of different samples was measured at 10^4 Hz. The molar ratio at O/AN=1.7 shows the highest conductivity at 23.14 mS/cm. PANI conductivities showed a variation with different molar ratios, as shown in Fig. 5. The conductivities for PANI samples are 8.75, 6.09, 10.81, 18.99, 23.14, and 5.11 mS/cm for O/AN molar ratios 0.5, 1, 1.25, 1.4, 1.7 and 2, respectively. The conductivity was decreased because when the molar ratio is overdose and exceed (O/AN= 1.7), this leads to the rupture of polymer chain due to the excessive oxidation of aniline [35]. The recommended condition to achieve both high productivity and conductivity is at molar ratio (O/AN= 1.7) as the high yield of PANI 128.44 % and conductivity of 23.14 mS/cm.

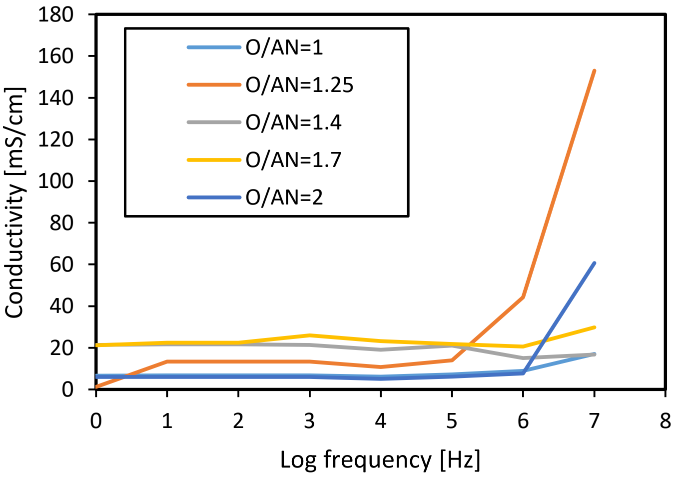


Fig. 6: Conductivity vs. log frequency plot for polyaniline samples at different (O/AN) molar ratio from 1 to 2.

3.2. Effect of dopant type on the productivity and conductivity

Different dopant acids (HCl, H_2SO_4, and H_3PO_4) were used in this study to examine the suitable dopant used in aniline's chemical oxidative polymerization. Using of different concentrations of acid dopants revealed a disparity of product amount and conductivity of polyaniline produced, as shown in Table 2. At a concentration of 0.5 M HCl, the addition of a little dopant produced a low conductivity value of 2.20 mS/cm. while at 1 M, the conductivity value increased to 6.10 mS/cm, which gives maximum conversion of aniline to polyaniline 127.79 % compared with other samples of HCl dopant. Then, the higher conductivity obtained is 36.20 mS/cm at 1.5 M HCl, as shown in Fig. 7 and 8. Using sulfuric acid dopant, the results showed a decrease in conductivity with increasing molarity of dopant. The usage of weak acid like phosphoric acid produced higher yields than HCl and H_2SO_4. The conductivity increased with an increase the concentration of H_3PO_4 and showed high conductivity at 2 M was 49.30 mS/cm. We would obtain 1.50 g of PANI/ 1 gm monomer if one molecule of phosphoric acid were protonated for each imine nitrogen in the base. Frequently, the yields are substantially higherexplaining the higher yield of H_3PO_4 samples [36].

In the case of HCl and H_2SO_4 dopant acids, the increase in the concentration of the acid (above 1.5 M) lead to the decrease of conductivity due to the degree of protonation, structural change, over oxidation and counter ion effect. The conductivity of PANI is strongly dependent on the degree of protonation of the polymer backbone. At lower acid concentrations, the PANI chains are partially protonated, which results in higher conductivity due to the increased charge carrier mobility. As the acid concentration (molarity) increases, the PANI chains become more heavily protonated, decreasing the overall conductivity [32].

The increased acid concentration can induce structural changes in the PANI polymer, such as the formation of more compact and rigid structures. These structural changes can reduce the overall chain mobility and disrupt the efficient charge transport along the PANI backbone, resulting in lower conductivity [37]. At very high acid concentrations, the oxidative polymerization conditions can become too aggressive, leading to the overoxidation of PANI. Overoxidation can introduce defects, chain scissions, or the formation of non-conducting byproducts, all of which can contribute to the decrease in conductivity [38]. The type and concentration of the counter ions (anions) present in the acid solution can also influence the conductivity of PANI. Certain counter ions may interact more strongly with the PANI chains, leading to increased charge carrier localization and reduced mobility. As the acid concentration increases, the concentration of these counterions may also increase, further reducing the conductivity.

Table 2: The effect of Dopant concentration on the yield and conductivity of PANI samples at O/AN =1.7.

Dopant type	**Acid dopant Concentration (M)**	**Yield (g)**	**Conductivity (mS/cm)**
HCl	0.5	5.34	2.20
	0.7	5.77	2.10
	1	5.98	6.10
	1.2	5.8	9.10
	1.5	5.43	36.20
	2	5.04	27.70
H_2SO_4	0.5	5.44	74.80
	0.7	5.35	52.00
	1	5.50	24.30
	1.2	5.70	26.60
	1.5	5.88	27.70
	2	5.60	5.80
H_3PO_4	0.5	6.22	1.60
	0.7	6.80	2.20
	1	7.17	2.40
	1.2	7.02	4.10
	1.5	6.60	5.90
	2	6.61	49.30

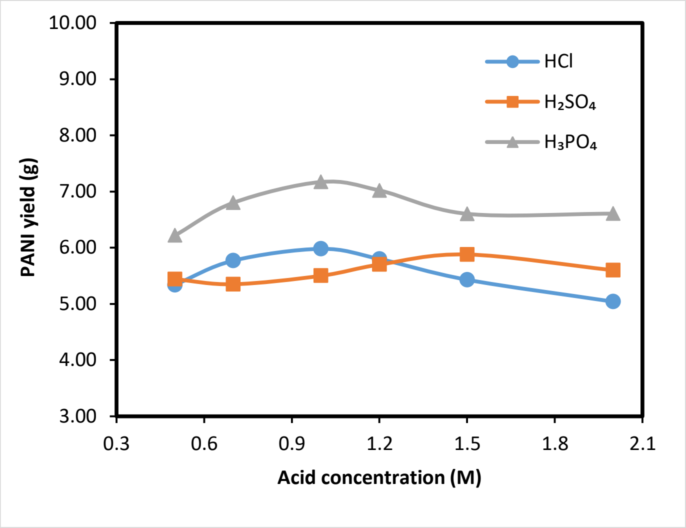


Fig. 7: The effect of dopant concentrations on yield of PANI samples.

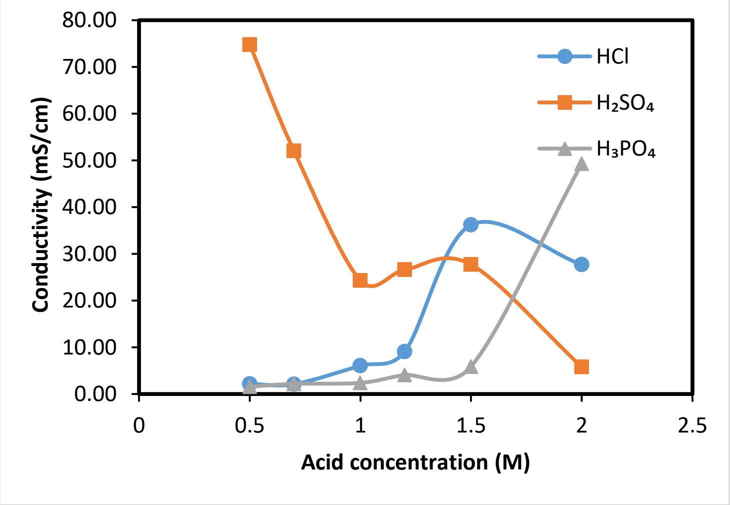


Fig. 8: The effect of dopant concentrations on conductivity of PANI samples.

While in case of H_3PO_4 acid, the increase in acid concentration led to increased conductivity. The reason that H_3PO_4 is a weaker acid compared to strong mineral acids like hydrochloric acid (HCl) or sulfuric acid (H_2SO_4). The proton doping of PANI by phosphoric acid is more reversible and controllable, allowing for a greater degree of protonation without causing over-oxidation. This controlled protonation can increase charge carrier concentration and mobility, resulting in higher conductivity [39]. These findings can be demonstrated according to the conventional concept of protonation, PANI "emeraldine salt" is formed when the acid combines with the imine 'nitrogen's in PANI (emeraldine) base. Two electrons from the electron pairs at the imine nitrogen are injected into the adjacent quinonoid ring as a result of the protonation of the imine nitrogen's, converting it to the benzenoid form.

Two cation-radicals on imine 'nitrogen's (unpaired electrons) are responsible for charge carriers during electrical conduction. Consequently, the imine 'nitrogen's that have received more protonation, the higher conductivity produced [36]. Additionally, the phosphate counter ions ($H_2PO_4^-$ and HPO_4^{2-}) interact with the PANI chains to enhance charge delocalization and transport, facilitating higher conductivity. The presence of phosphoric acid can also induce structural changes in PANI, such as forming more linear and extended polymer chains, further improving the conjugation and charge transport properties [30].

The highest yield at each dopant was observed at 1 M HCl (127.79%), 1.5 M H_2SO_4 (126.29%) and 1 M H_3PO_4 (153.99%). The results revealed that the highest yield was achieved despite using weak acid of H_3PO_4, moreover, there is little difference between both yields produced using HCl and H_2SO_4 dopants. The highest conductivities were detected at concentrations of 1.5 M HCl (36.20 mS/cm), 0.5 M H_2SO_4 (74.80 mS/Cm), and 2 M H_3PO_4 (49.3 mS/Cm).

The reason for increasing the yield above 100% in all PANI samples is the existence of counter ions like sulfonate anion [40]. Also at lower reaction temperatures 0-5°C, PANI is produced in high molar mass that can increase the yield of PANI. However, molar mass has no great effect on the conductivity of the polymer [41]. This is consistent with prior research that produced high yield of PANI preparations exceeding 100%. [35-36].

In Fig. 8 it was observed that the conductivity was obtained at a low concentration of H_2SO_4 (0.5 M). This can be interpreted due to the high dissociation of H_2SO_4 to produce 2 H^+.

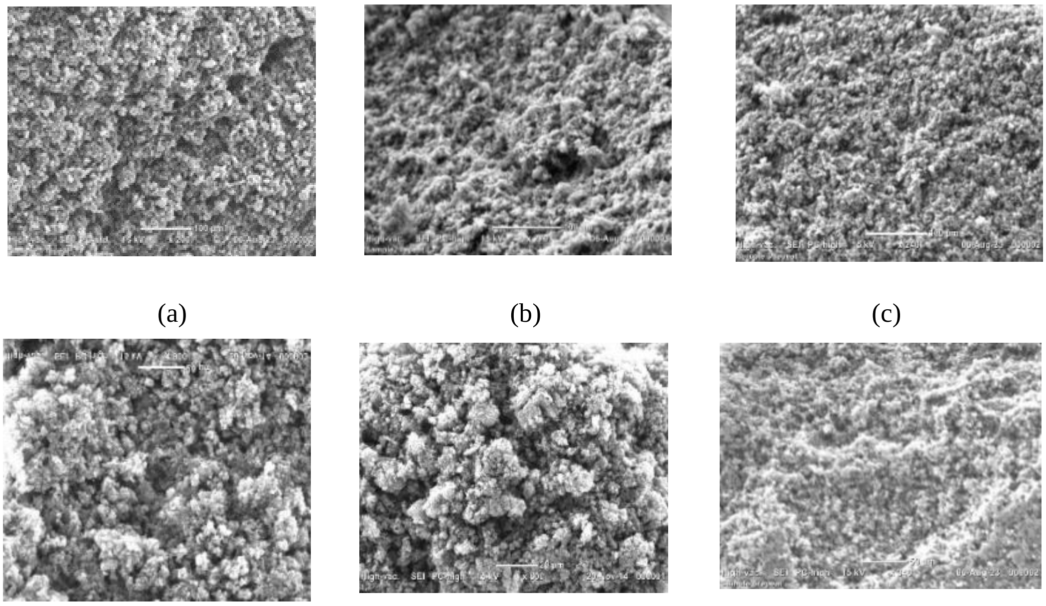
$$H_2SO_4 \rightleftarrows 2H^+ + SO4^{2-}$$

Moreover, the low concentration of H_2SO_4 is considered safer and more suitable for polyaniline formation and protonation. Furthermore, the high concentration of H_2SO_4 dopants may lead to aggressive conditions during the polymerization reaction, so low conductivity was produced at high concentrations (1-2 M). HCl has low protonation less than H_2SO_4 in spite of the high dissociation. So, low conductivity was expected, but it slightly improved with increasing concentration. H_3PO_4 has low dissociation, although it has 3 protons, so it was low conductivity, but it improved with high concentration.

3.3. SEM and EDX analysis

The morphology of prepared polyaniline samples is shown in Figures 9 and 10, where the presence of homogeneous fine particles is revealed. EDX studies calculated the mass percentage of each sample of PANI, as shown in Table 3. The data studied the effect of O/AN molar ratio on the mass percentage of each element that exist in the PANI samples. Chloride ion was detected with small content (0.71-1,69%) due to using of HCl as a dopant (0.5 to 2M HCl) .The results of the elemental analysis show that PANI contains oxygen in all samples, which might be explained by the oxygen that is firmly adsorbed on PANI.

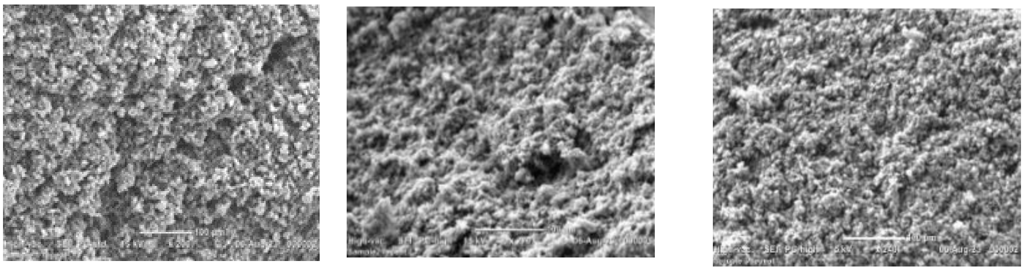
This could be caused by partially oxidized PANI chains or, most likely, bound water molecules, which agrees with other references [32,44]. EDX results showed that prepared PANI samples containing the main elements of C, N and the appearance of other elements like O may due to a high concentration of oxidant, and it is easily adsorbed as water molecules at the PANI surface. While other elements like S and Cl may appear due to the usage of dopants H_2SO_4 and HCl.



(a) (b) (c)

(d) (e) (f)

Fig. 9 : SEM photos of PANI prepared using HCl dopant and different O/AN molar ratios (a) 0.5 (b) 1 (c) 1.25 (d) 1.4 (e) 1.7 (f) 2.



(a) (b) (c)

Fig. 10 : SEM photos of PANI prepared with different dopants: (a) 1.5 M HCl, (b) 0.5 M H_2SO_4 , and (c) 2 M H_3PO_4.

Table 3: The mass percent of elements in PANI samples from EDX analysis.

Oxidant	**O/AN molar ratio**	**Mass percent of elements**				
		C %	**N%**	**O%**	**S%**	**Cl%**
APS	0.5	43.18	26.9	24.85	2.449	2.51
	1	41	31.48	24.18	2.263	1.587
	1.25	42.73	29.57	23.59	2.41	1.696
	1.4	40.41	33.27	23.34	2.17	0.81
	1.7	40.44	34.2	22.14	2.3	0.92
	2	41.1	32.22	23.38	1.603	1.686
Dopant type	**Dopant Conc. (M)**					
HCl	0.5	43.6	30.79	22	2.88	0.716
	1	42.73	29.57	23.59	2.41	1.696
	1.5	44.95	30.65	19.26	3.28	2.77
	2	43.32	33.72	19.4	2.03	1.513
H_2SO_4	0.5	42.81	29.98	24.50	2.71	-
	1	41.31	29.32	21.77	4.26	-
	1.5	42.01	31.24	19.34	3.74	-
	2	42.50	29.34	24.45	3.70	-
H_3PO_4	0.5	41.79	34.73	20.7	2.78	-
	1	40.87	31.84	23.91	3.37	-
	1.5	43.29	33.3	19.85	3.57	-
	2	41.5	33.44	21.97	3.08	-

3.4. FTIR analysis

A diagram of chemical formulas of Emeraldine salt (dark green powder) form the vibration bond wave numbers of prepared samples are shown in Fig. 11. FTIR graphs were conducted to study the formation of polyaniline using different molar ratio of oxidant to aniline from 0.5 to 2. The characteristics peaks of PANI from 0.5 to 2 molar ratio include peaks from 3045 to 3052 cm^{-1} and from to 3203 to 3221 cm^{-1} corresponding to (N–H stretching vibrations of secondary amine) and sharp peaks ranges (1551-1556 cm-1) to (C=C stretching of quinoid ring (N=Q=N)), from 1452 to 1472 cm^{-1} ((C=C stretching vibration of benzenoid ring (N-B-N)) and Peaks range (1236 to 1292 cm^{-1}) attributed to (C - N stretching of secondary aromatic ring).

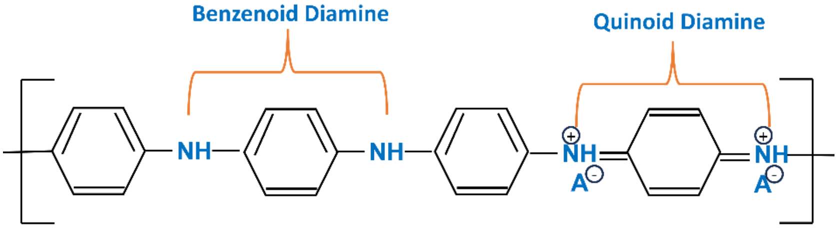


Fig. 11: A diagram of chemical formula of PANI emeraldine salt form.

The peaks from 670 to 791 cm^{-1} represented Aromatic C–H out-of-plane bending vibrations. The peaks from 1024 to 1038 cm^{-1} are for the vibrations bending of aromatic C–H in-plane. These date are matching with other literature [45,46]. The 571 to 577 cm-1 peaks may be attributed to C-Cl stretching [46]. The Peaks of O/AN molar ratio peaks are listed in Table 4. Furthermore, in Fig. 12 displays the FTIR graphs for O/AN molar ratio (a) 0.5 (b) 1 (c) 1.25 (d) 1.7 (e) 2. All the samples confirmed the formation of the PANI conductive (emeraldine salt) structure.

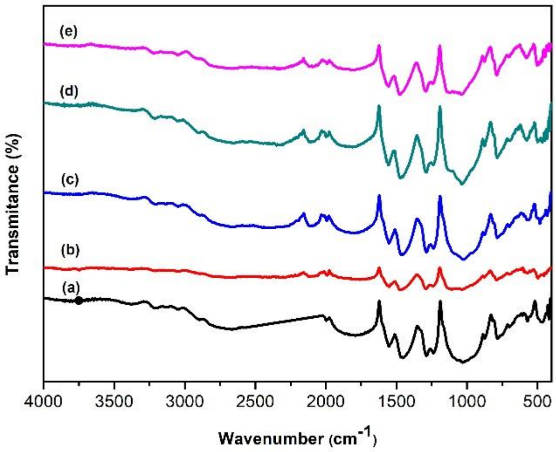


Fig. 12: FTIR graphs for PANI prepared at O/AN molar ratios (a) 0.5, (b) 1, (c) 1.25, (d) 1.7, and (e) 2.

FTIR peaks for HCl, H_2SO_4, and H_3PO_4 dopants (different concentrations) also confirmed the formation of emeraldine salt in all samples, as shown in Fig. 13. For PANI samples doped with HCL, the samples showed peaks at 696 and 786 cm^{-1} represented for Aromatic C–H out-of-plane bending vibrations. The aromatic C–H vibrations bending in-plane has a peak at 1036 cm^{-1}. The peaks for C – N stretching of secondary aromatic ring found at 1230 to 1296 cm^{-1}. Stretching vibration of the benzenoid (B) ring (N-B-N) at 1475 cm^{-1} for C=C is observed. C=C stretching of quinoid (Q) ring(N=Q=N) displayed at 1545 cm^{-1}. Two peaks for N–H stretching vibrations of secondary amine are visible at 3047 and 3213 cm^{-1}. The band that appeared at 578 cm^{-1} may attributed to C-Cl stretching. The samples doped with H_2SO_4 showed peaks at 705 and 777 cm^{-1} represented for Aromatic C–H out-of-plane bending vibrations. The aromatic C–H vibrations bending in-plane have a peak at 1020 cm-1.

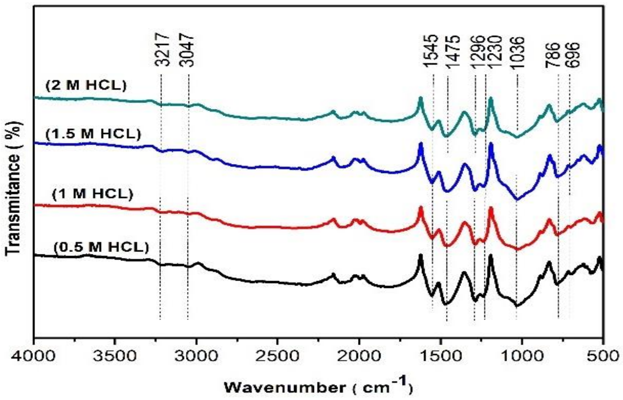
The secondary aromatic ring's C-N stretching peaks are located at 1241 and 1287 cm-1. Stretching vibration of the benzenoid (B) ring (N-B-N) at 1456 cm-1 for C=C is observed. At 1553 cm-1, the quinoid (Q) ring (N=Q=N) exhibits a C=C stretching. There were two peaks visible at 3039 and 3217 cm-1 from the secondary amine's N–H stretching vibrations. According to other research, the peak at 563 might stand for sulfate counter ions [47]. The H_3PO_4 doped samples showed peaks at 698 and 779 cm^{-1} represented for Aromatic C–H out-of-plane bending vibrations. The peak at 1033 cm^{-1} is for the vibrations bending of aromatic C–H in-plane. The peaks for C – N stretching of the secondary aromatic ring at 1230 to 1241 cm^{-1}. For C=C stretching vibration of the benzenoid (B) ring (N-B-N) was observed at 1458 cm^{-1}. C=C stretching of quinoid (Q) ring(N=Q=N) displayed at 1562 cm^{-1}. Two peaks from N–H stretching vibrations of secondary amine were shown at 3052 and 3213 cm^{-1}.

3.5. XRD analysis

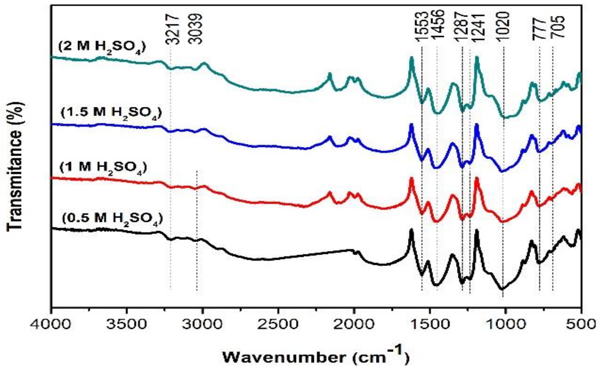
PANI samples have both crystalline and amorphous regions due to the presence of benzenoid and quinonoid groups [48]. The samples have peaks at 2θ=25.27° and 20.53°, confirming emeraldine salt structure formation as shown in Fig.14 [49]. The XRD results show that H_2SO_4 and HCl doped acids showed more crystalline structure (sharp peaks) than H_3PO_4.

Table 4: The chemical bonds of PANI were obtained from FTIR studies

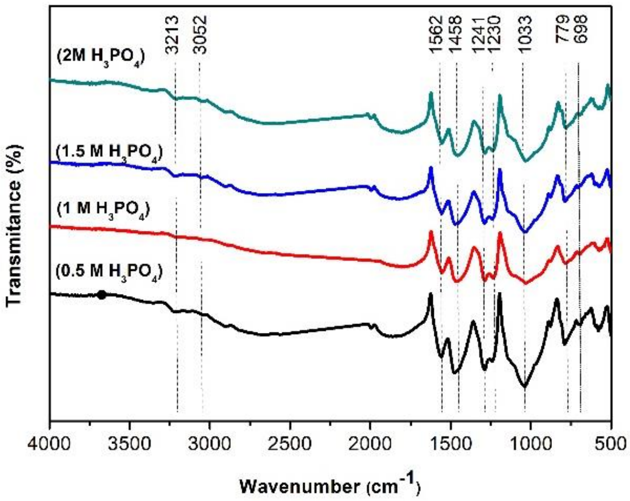
FTIR Assignment	Oxidant/aniline molar ratio					
	Vibration bond range (cm^{-1})	0.5	1	1.25	1.7	2
Aromatic C–H out-of-plane bending vibrations	600-900	698-785	694-789	696-783	670-785	700-791
Aromatic C–H in-plane bending vibrations	1000-1180	1032	1030-1117	1024	1034	1038-1134
C – N stretching of secondary aromatic ring.	1200-1300	1288	1236-1288	1244-1284	1236-1292	1289
C=C stretching vibration of benzenoid (B) ring (N-B-N)	1400-1480	1452	1464	1452	1472	1470
C=C stretching of quinoid (Q) ring(N=Q=N)	1500-1600	1554	1554	1551	1555	1556
N–H stretching vibrations of secondary amine	3000-3500	3052-3211	3045-3211	3045-3203	3047-3215	3055-3221
C-Cl stretching	550-850	571	573	575	577	571



(a)



(b)



(c)

Fig. 13: FTIR graphs for different dopant concentrations (a) HCl, (b) H_2SO_4, and (c) H_3PO_4.

3.6. Empirical correlations by regression analysis

The mathematical models to describe the relationship between the effect of the O/AN (X) molar ratio on PANI yield (Y) and conductivity (C) S/cm produced is generated using regression analysis as described below in the equations (1) and (2):

$$Y = 10.369 \times X^4 - 56.712 \times X^3 + 105.34 \times X^2 - 74.092 \times X + 19.553 \qquad R^2 = 0.997 \qquad \text{Eq. (1)}$$

$$C = -0.0513 \times X^4 + 0.191 \times X^3 - 0.2161 \times X^2 - 0.0799 \times X + 0.0022 \qquad R^2 = 0.984 \qquad \text{Eq. (2)}$$

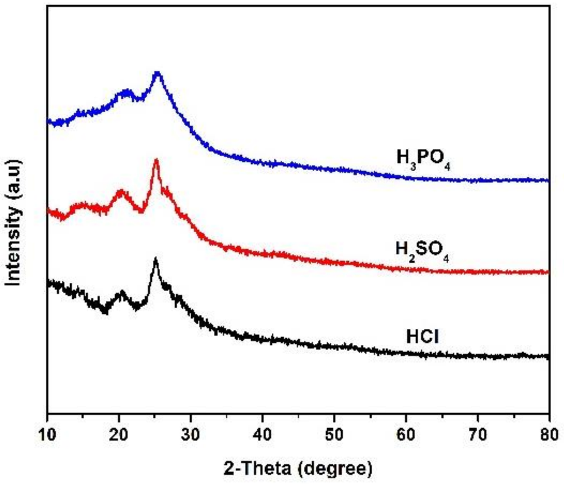


Fig. 14: XRD graph of PANI samples at 1.5 M HCl, 0.5 M H_2SO_4, and 2 M H_3PO_4.

Other equations were generated to correlate the effect of acid concentration (A) on PANI conductivity for each acid type using equations (3-5).

For HCl acid:

$$Y = 1.6846 \times A^3 - 7.3332 \times A^2 + 9.2951 \times A + 2.305 \qquad R^2 = 0.997 \qquad \text{Eq.}(3)$$

$$C = -0.1477 \times X^4 + 0.6447 \times A^3 - 0.9496 \times A^2 + 0.5763 \times A - 0.1203 \qquad R^2 = 0.985 \qquad \text{Eq.}(4)$$

For H_2SO_4:

$$\mathrm{Y} = -1.3329 \times \mathrm{A}^3 + 4.6323 \times \mathrm{A}^2 - 4.4741 \times \mathrm{A} + 6.6802 \qquad \mathrm{R}^2 = 0.995 \qquad \text{Eq.}(5)$$

$$\mathrm{C} = -0.0869 \times \mathrm{A}^3 + 0.3532 \times \mathrm{A}^2 - 0.4741 \times \mathrm{A} + 0.2362 \qquad \mathrm{R}^2 = 0.986 \qquad \text{Eq.}(6)$$

For H_3PO_4:

$$Y = 2.547 \times A^3 - 10.524 \times A^2 + 12.212 \times A + 1.8973 \qquad R^2 = 0.987 \qquad Eq.(7)$$

$$C = 0.0461 \times A^3 + -0.1328 \times A^2 + 0.129 \times A - 0.0326 \qquad R^2 = 0.996 \qquad Eq.(8)$$

The polynomial regression analysis revealed the great effect of the reaction parameters O/AN, molar ratio, acid type and concentration in preparing PANI productivity and conductivity properties. The R^2 values (the coefficient of determination) showed a good fitting model of the data as R^2 values are closer to 1.

4. Conclusion

Polyaniline was successfully prepared to produce dark green emeraldine salt of high conductivity. The effect of different APS/AN molar ratios on the product and conductivity was studied using 1 M HCl dopant. The highest molar ratio was 1.7, with a high conductivity of 23.14 mS/cm. Moreover, the effect of using various protonic dopants, mono, di, and tri-protonic acids (HCl, H_2SO_4, H_3PO_4) and also varying concentrations from 0.5 to 2 M were investigated. PANI of the highest conductivities 36.20, 74.80, and 49.3 mS/cm, was produced using different acid concentrations 1.5 M HCl, 0.5 M H_2SO_4, and 2 M H_3PO_4, respectively. H_3PO_4 showed a higher yield, 7.17 g, when compared with other dopants. The study revealed that the degree of protonation, structural change, over oxidation and counter ion effect were highly influenced with acid type and concentration. SEM analysis showed that the morphology of the prepared PANI has homogeneous and very fine particles.

The chemical compositions of samples, according to EDX, contained mainly C, N, O, S, and other anions like Cl that appeared in the samples that were doped with HCl. FTIR confirmed that the produced PANI was prepared in the form of a conductive emeraldine salt structure (dark green color). Regression analysis reveals that the mathematical model correlations between O/AN or acid concentration on productivity and conductivity are highly effective. This is demonstrated by the good agreement between theoretically obtained conductivity values under various reaction conditions and the experimentally obtained conductivity under the same conditions.

Conflicts of interest

The authors have no conflict of interest.

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