

THE INTERNATIONAL JOURNAL OF SCIENCE & TECHNOLEDGE

Study of FTIR Spectra and Effect of Transitions on Conductivity of Polyaniline Synthesized Using Different Dopants by Chemical Oxidation

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Abstract:

This article reports the synthesis of Polyaniline (PANI) in emeraldine form (EB) by in-situ chemical oxidation method using different dopants and ammonium persulphate (APS) as an oxidant. The samples were characterized by FTIR, UV-Vis, and their conductivity determined by four-point probe method. Quinoid and benzenoid bands at $1553\text{-}1596\text{ cm}^{-1}$ and $1437\text{ - }1496\text{ cm}^{-1}$ respectively were observed in all the samples. The band gaps and conductivity values for all the bulk samples were obtained using the absorption spectra and Stern relation. It was found that the transition $\pi - \pi^$ for PANI- H_2SO_4 occurs earlier than in PANI-HCl sample. This can only be as a result of the H_2SO_4 acid been a stronger acid than the HCl and as a result the transition from $\pi - \pi^*$ required lower wavelength for PANI- H_2SO_4 sample as compared to the PANI-HCl sample. By comparing the four samples the $\pi - \pi^*$ transition then can be arranged from the strongest to the weakest as PANI- H_2SO_4 followed by PANI-HCl then PANI- HNO_3 and the weakest being PANI- CH_3COOH . The same trend is also observed for electrical conductivity of these samples.*

Keywords: PANI, Band gap, UV-Vis Spectra, chemical oxidation, FTIR spectra

1. Introduction

Polymers are a class of materials that are important to our everyday life. Cabinets, plastic cutlery and latex paints are examples of polymers that are used every day. They are giant molecules of high molecular weight which are built up by linking together large numbers of smaller molecules called monomers. The reaction by which the monomers combine to form a huge polymer is known as polymerization (Gowariker et al., 1986). Traditionally polymers were thought of as insulators when it comes to its applications in electronics. In the mid-19th century scientist conducted research into some organic based polymers for their application in electronics (Inzelt, 2008). In the case of polypyrrole it was observed that it had resistivity as low as 1 ohm/cm (Bolto et al., 1963). (Songxi, 2012) cites multiple reports of similar high conductivity oxidized polyacetylenes. DeSurville and coworkers reported high conductivity in polyaniline (De Surville et al., 1968). Hideki Shirikawa, Alan MacDiarmid and Alan J. Heeger in 1977 published a paper on the high conductivity in oxidized iodine-doped polyacetylene (Shirikawa et al., 1977). They were awarded the 2000 Nobel Prize in Chemistry for the discovery and development of conductive polymers (Natarajah, 2012).

Lightfoot's studies on the oxidation of aniline in 1860s led to the discovery of polyaniline (MacDiarmid, 2001). The first definitive report of polyaniline did not occur until 1862, which included an electrochemical method for the determination of small quantities of aniline (Letheby, 1862). Only since the early 1980s has polyaniline captured the intense attention of the scientific community. This interest is due to the rediscovery of high electrical conductivity. Amongst the family of conducting polymers and organic semiconductors, polyaniline has many attractive processing properties (Pandya, 2016). Polyaniline (PANI) is one of the most studied conjugated polymers due to its widely tunable electrical conductivity (Cao et al., 1992) and environmental stability (Rannou and Nechtschein, 1997, DeLongchamp and Hammond, 2001). PANI can be readily synthesized from commercially available starting materials under mild conditions by oxidation methods (Masters et al., 1991), (Wei et al., 1989). Polyaniline remains one of the most interesting materials due to its unique conduction mechanism and good environmental stability in the presence of oxygen and water (Kumar et.

al.,1997).

2. Methodology

2.1. Synthesis of Polyaniline (PANI)

12.03 g of $(\text{NH}_2)_2\text{S}_2\text{O}_8$ was measured and put in 600 ml beaker. 5.00 g of the aniline monomer was measured into a 500 ml beaker. Ammonium persulphate solution (APS) was formed by adding 70 ml of H_2SO_4 to it. 75 ml of H_2SO_4 was poured into the aniline monomer. Drop-wise addition of aniline to the APS solution was done. Change in the colour of the solution was observed after 10 minutes. The colour of the solution changed from whitish-brown to pale green then green (emeraldine salt). The solution was left for 12 hours for complete polymerization to occur.

Similarly, samples of polyaniline doped with Nitric acid (HNO_3), Hydrochloric acid (HCl), and Acetic acid (CH_3COOH) were prepared. Each of the Emeraldine salt formed was filtered by continuously washing with the acid until the filtrate was clear. The samples were dried at 70°C in an oven and crushed into powder form. For each sample, some of the powder washard pressed into pellet using a metallic mold.

2.2. Characterization

2.2.1. FTIR Spectra

Perkin Elmer Spectrum Version 10.08.09 was used to carry out the FTIR for the samples dried at 70°C . Below is the table for the absorption observed for each sample.

SAMPLE	N-H stretching	C-H stretching	C = N stretching	Quinoid Bond	Benzenoid Bond	C-H out of plane
HCl	3750	3053	1644	1596	1496	800
H_2SO_4	3787	-	1650	1559	1473	800
HNO_3	3787	3060	1647	1544	1437	824
CH_3COOH	-	-	-	1559	1473	877

Table 1: Fourier Transformation Infrared Spectroscopy of the Bulk Samples

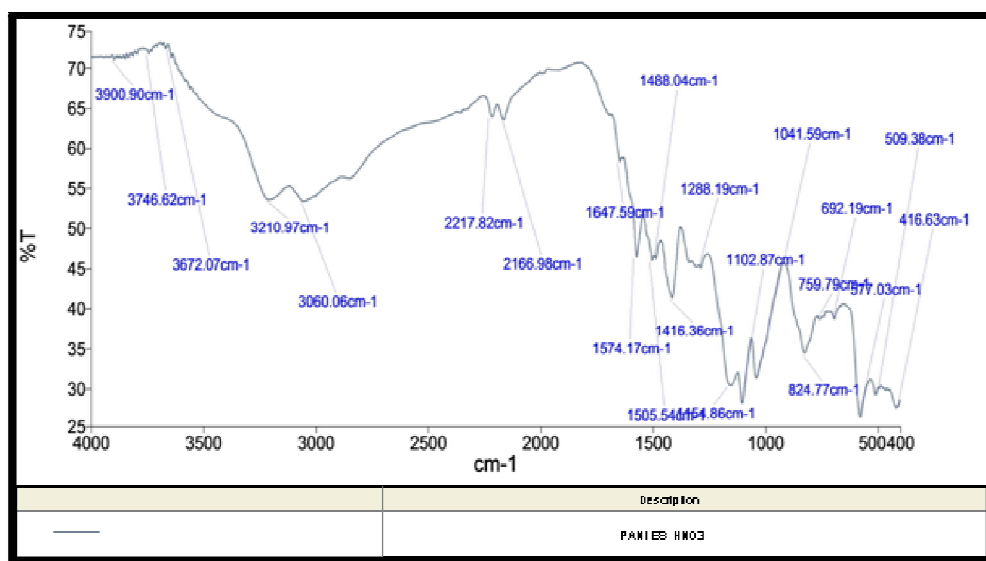


Figure 1: FTIR of PANI- HNO_3 Bulk Sample

Fig. 1 above shows the FTIR for the PANI- HNO_3 sample. The most significant bands for a protonated sample were observed in the bands at 1574.17 cm^{-1} and 1488 cm^{-1} . The ring-stretching vibrations of the quinonoid and benzenoid rings of aniline can be attributed to the 1574.17 cm^{-1} and 1488 cm^{-1} bands respectively. The band at 3060 cm^{-1} is due to the C-H stretching aromatics which is very strong. There was a weak C=N stretching band at the 2217.82 cm^{-1} . The mono substituted benzene is a clear characteristic observed in the absorption peak at 1041.59 cm^{-1} . The band at 824.77 cm^{-1} was attributed to the out of plane C-H bending.

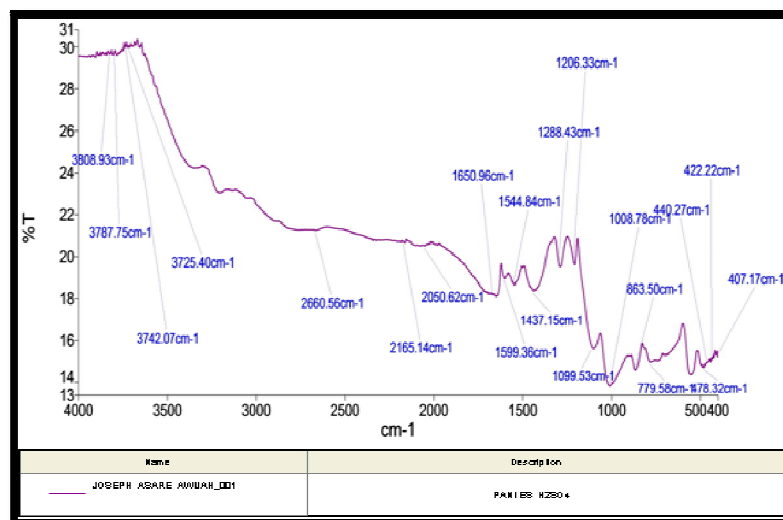


Figure 2: FTIR of PANI-H₂SO₄ Bulk Sample

The bands at 3742.7 cm⁻¹ and 3787.75 cm⁻¹ are attributed to hydrogen-bonded N-H stretching. The wavenumbers 2660.56 cm⁻¹, 2165.14 cm⁻¹ and 2050.62 cm⁻¹ are due to absorption of free charge- carriers in the protonated polymer. The quinonoid and benzenoid ring-stretching vibrations were at the 1544.84. A blue shift can be observed for the quinonoid caused be the vibrations at the previous frequency to 1599.36 cm⁻¹ the band at 863.50 cm⁻¹ in the spectrum of the protonated sample represents the H₂SO₄ – counterion.

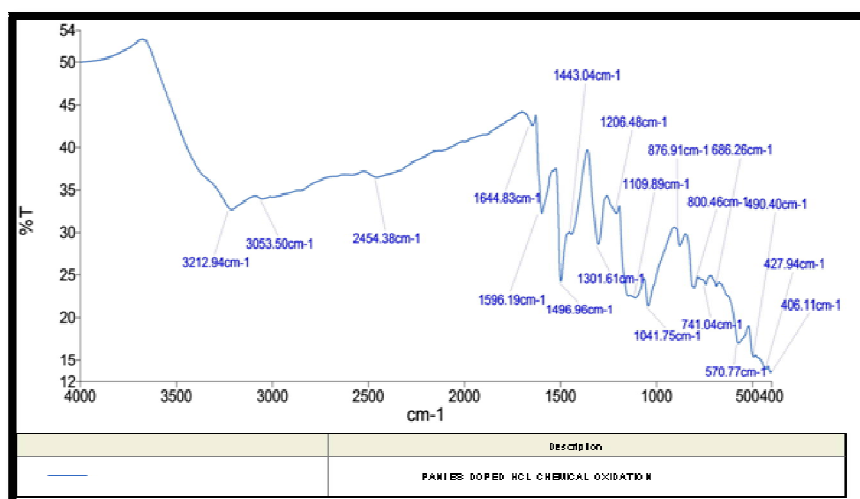


Figure 3: FTIR of PANI-HCl Bulk Sample

The figure above, Fig. 3 shows the IR of PANI-HCl sample. The bands at 3212.94 cm⁻¹ and 3053.50 cm⁻¹ are attributed to hydrogen-bonded N-H stretching and the aromatic C-H stretching. The bands at 1596.19 cm⁻¹ and 1496 cm⁻¹ can be attributed to the quinonoid and benzoid structure of PANI cm⁻¹ in the spectrum of the sample corresponds to the π -electron delocalized induced in the polymer by protonation. The band observed at 1206.48 cm⁻¹ is a characteristic of the conducting protonated form of PANI.

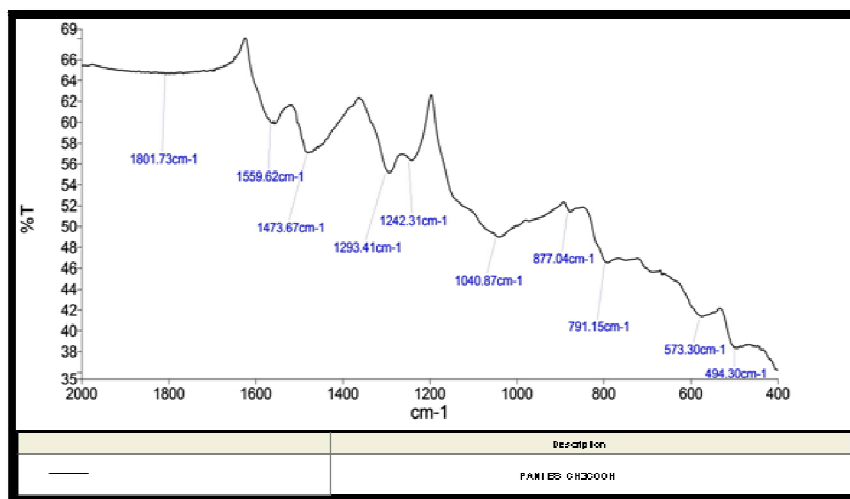


Figure 4: FTIR of PANI-CH₃COOH Bulk Sample

The quinoid and benzenoid ring-stretching were found at the 1559.62 cm⁻¹ and 1473.67 cm⁻¹ respectively. The band characteristic of conducting protonated form was observed at 1242.62 cm⁻¹. The 877.04 cm⁻¹ band can be attributed to the C-H out of plane bending vibrations of hydrogen atoms. Bands at 1559 cm⁻¹ and 1473 cm⁻¹ are assigned to quinoid and benzenoid respectively for PANI-CH₃COOH. The same bands were observed for PANI-H₂SO₄. The ratio of IQ/IB can be used to estimate the degree of oxidation state. The similarities observed in these two samples point to the fact that the oxidation degree in the two dopants is the same. The IQ/IB ratio for PANI-HCl and PANI-HNO₃ samples were not the same in comparison to any of the samples. This indicates that these samples had different degrees of oxidation (Melad et al., 2016). According to (Atassi et al., 2008) band characteristics of protonated form of PANI is observed at 1246 cm⁻¹ and this has been interpreted as originating from bi-polaron structures related to C-N stretching vibration. In this work bands at 1288 cm⁻¹, 1206 cm⁻¹, 1242 cm⁻¹ and 1206 cm⁻¹ were observed for PANI-HNO₃, PANI-H₂SO₄, PANI-CH₃COOH and PANI-HCl respectively. Also peaks at 1580 cm⁻¹ have been reported to confirm the presence of a protonated imine function (Rao et al., 2000). PANI-HNO₃, PANI-H₂SO₄, PANI-CH₃COOH and PANI-HCl the peaks recording around this band were 1574 cm⁻¹, 1544 cm⁻¹, 1559 cm⁻¹ and 1598 cm⁻¹ respectively.

2.2.2. UV-Vis spectra

The absorption bands observed are usually within the ranges of 290-324, 402-430 and 828-835nm for a pure PANI (Owusu-Sekyere et al., 2017). The figure below shows a block diagram of optical detection systems of bulk samples of polyaniline using the various acids employed in this experiment. There are some bands that are characteristics of polyaniline.

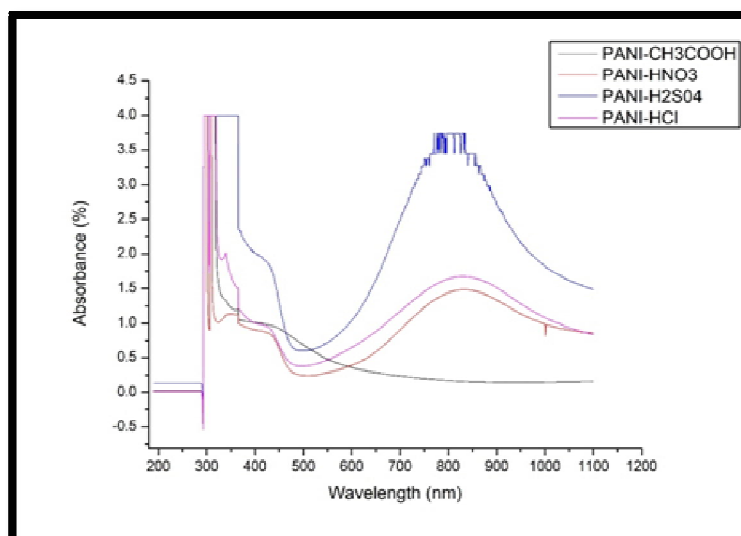


Figure 5: Absorbance versus Wavelength of Bulk Samples

The bands observed in all the four samples are in the stated ranges according to literature. For the weak acids PANI-CH₃COOH, the bands observed are in the range of 350-365, 430-440 and 770-800 nm. The

polaron and bipolaron bands which are clear characteristics of PANI can be seen in the range for the acetic acid. Similarly, the bands in PANI-HNO₃ appears in the ranges of 335-360 nm which is attributed to the $\pi - \pi^*$ electron transition, polaron is observed in the 410-440 nm band and 700-800 nm been the band for transition between benzenoid-quinoid rings. Among the two weak acids it was observed that for HNO₃ the bands stretched further as compared to that of the acetic acid.

The bands that appear in the PANI-HCl sample were 310-400 nm, 420- 440 nm which show the presence of polarons and bipolarons transitions and the 700-810 nm band which can be attributed to charge transfers from the benzenoid and quinoid rings. In the same way these bands appeared in the PANI-H₂SO₄ sample. The absorption bands that have been obtained from the UV-Visible spectra are in good agreement with that reported in the literature.

Although the samples synthesized using different aqueous acids did show the various bands characteristic of PANI. Some comparisons can be made in terms of the bands and how they appeared via the spectral lines for each sample. To begin with are PANI-CH₃COOH and PANI-HNO₃. Although the transition in both occurs within the same band the difference in the wavelength could possibly be as results of the electron making a bigger jump from the pi bonding to pi anti-bonding state in PANI-HNO₃. This scenario runs throughout the entire bands when comparing PANI-HNO₃ to PANI-CH₃COOH.

The transition of the pi bonding to the pi anti-bonding in PANI-H₂SO₄ occurs earlier than in PANI-HCl sample. This can only be as a results of the H₂SO₄ acid been a stronger acid than the HCl and as a result the transition from $\pi - \pi^*$ required lower wavelength for PANI-H₂SO₄ sample as compared to the PANI-HCl sample. By comparing the four samples the $\pi - \pi^*$ transition then can be arranged from the strongest to the weakest as PANI-H₂SO₄ followed by PANI-HCl then PANI-HNO₃ and the weakest been PANI-CH₃COOH.

2.3. Determination of the Band Gap of Bulk Samples

Using the Stern relation below (Stern, 1963), the energy band gaps (E_g) of the thin films were established by the absorbance spectra.

$$A = \frac{K(h\nu - E_g)^n}{h\nu} \quad (1)$$

Where $h\nu$ is the photon energy, A is the absorbance; K equals a constant while n carries the value of either 1 or 4. In a direct transition n is equal to 1 and 4 for allowed and forbidden transitions respectively. The band gap, E_g, were obtained from a straight line plot of $(Ah\nu)^2$ as a function of $h\nu$. Extrapolation of the line to intersect the horizontal axis at $(Ah\nu)^2 = 0$, gave the energy band gap as shown in the figures below. The E_g obtained were 3.30 eV, 3.75 eV, 3.83 eV and 3.89 eV for PANI-HCl, PANI-H₂SO₄, PANI-HNO₃ and PANI-CH₃COOH respectively.

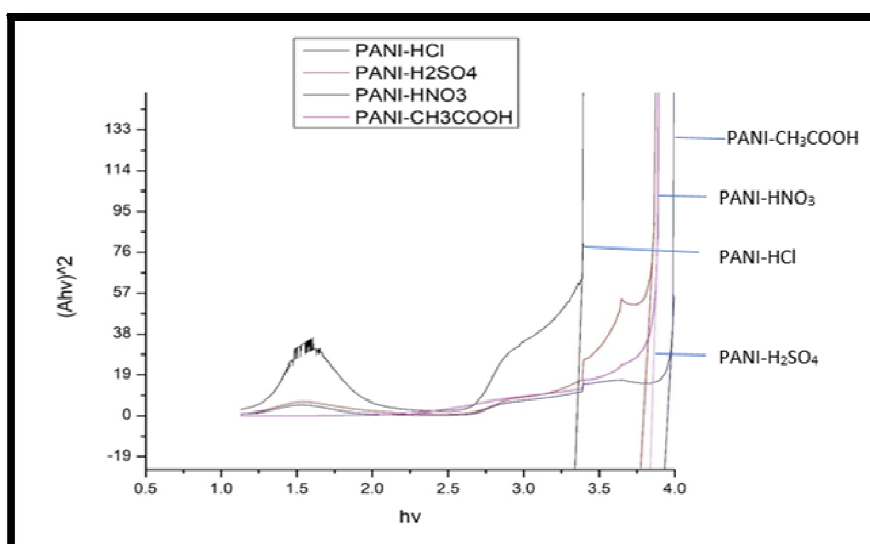


Figure 6: Band Gap of Bulk samples

SAMPLE	Bulk Sample (E _g /eV)
HCl	3.30
H ₂ SO ₄	3.75
HNO ₃	3.83
CH ₃ COOH	3.89

Table 2: Band Gap of Bulk Samples

2.4. Measurement of Electrical Conductivity

Using the four point probe requires the use of the equation below:

$$\rho = 4.5324t \frac{V}{I} \quad (2)$$

Where; ρ = resistivity of the material, the reciprocal which gives the DC conductivity, σ , since $\sigma = 1/\rho$
 I = Average current supplied to the entire set-up

V = Average voltage drop measured across the sample

t = thickness of the sample

DOPANT	AVERAGE CURRENT I/mA	AVERAGE VOLTAGE V/mV	$\rho / \Omega.cm$	$\sigma/ S.cm^{-1}$	$\sigma/ S.cm^{-1}$ from literature	Reference
HCl	1.95	2.00	1.956	0.669	0.16	(Sinha et al., 2016)
H ₂ SO ₄	2.35	1.00	0.578	1.183	1.09	(Alesary et al., 2018)
HNO ₃	0.35	0.70	2.719	0.300	0.04	(Manaf et al., 2017)
CH ₃ COOH	0.25	1.00	5.438	0.148	0.04	(Kulkarni et al., 2004).

Table 3: Electrical Conductivity

3. Conclusion

Polyaniline, PANI-ES was synthesized using four different dopants (HCl, H₂SO₄, HNO₃ and CH₃COOH). The method of synthesis was chemical oxidation. UV-Vis spectroscopy was carried out on the samples prepared by the method stated. Absorption peak was observed between the range 300-350 nm which depicts the $\pi - \pi^*$ electron transition. Another peak between 450 – 540 nm was also noticed for in all the samples and can be attributed to the polaron and bipolaron transition in polyaniline. A conductivity of 1.183 S/cm was observed for polyaniline doped with H₂SO₄ and it can be ascribed to the electron transfer in the structure as obtained from the UV-Vis analysis. HCl and HNO₃ acid doped samples resulted in moderate conductivity while the CH₃COOH doped sample had the least conductivity which might be due to the decrease in localized defect states in the polaron band as observed from $\pi - \pi^*$ transitions.

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