

SYNTHESIS AND STUDY OF ATR SPECTRA OF POLYANILINE/GRA NANOCOMPOSITES

O.A. Nunoo, E.K.K. Abavare, R.K. Nkum and K. Singh

Department of Physics

Kwame Nkrumah University of Science and Technology, Kumasi, Ghana (West Africa)

ABSTRACT

Nano composites are a particular class of materials resulting from combinations of two or more compounds by an appropriate method, which results in materials having unique physicochemical properties and large potential for application in diverse areas. Some of the distinctive properties of polymeric Nano composites can be derived from the successful combination of the uniqueness of the parent constituents into a particular polymer. These composites vary from the pure polymers in respect to some of the physical and chemical properties and hence are useful for many different applications. We synthesized Polyaniline (PANI) in Emeraldine form by chemical oxidation method using Ferric Chloride ($FeCl_3$) as a catalyst and Hydrogen peroxide (H_2O_2), as an oxidant. Simultaneous synthesis of polyaniline (PANI)/ GRA Nano composites was also done by the same chemical oxidation method. The characteristic absorption peaks of Attenuated Total Reflectance (ATR) spectra for GRA, PANI and PANI/GRA provide information about the changes in the chemical structure of PANI. ATR spectra also give indication that the incorporation of GRA in the matrix of PANI seems to be effective for the improvement of the physicochemical properties of the Polyaniline.

Key words: ATR Spectra, Polyaniline/GRA, Nano composites.

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1. INTRODUCTION

Among the conducting polymers, polyaniline (PANI) has emerged as the material of choice for many applications. PANI is the oldest organic polymer ever synthesized. The first report of polyaniline synthesis was recorded in 1862. Studies carried out in 1910-1911 identified that the molecular sequence involved alternating amine/imine and benzoid/quinoid parts [1]. The wider interest in polyaniline was because of several factors including some research results reporting that PANI exhibited long-standing electrical conductivity following introduction of its stable half-oxidized/half-reduced form called emeraldine base (EB) to a protonic acid [2]. Also Heeger, MacDiarmid and Shirakawa's Nobel Prize winning work that identified the

physical mechanisms of hole transport in conductive polymer systems [3] brought a new direction in the processing of conducting polymers.

Graphite (GRA) has been extensively studied [4] as it is used to increase the electrical conductivity of polymer matrices. Lei Wang et al. [5] prepared HClO₄-doped polyaniline/graphite composites by mechanical ball milling and cold pressing. Many researchers have attempted to convert p-type to n-type conduction in PANI matrix [5-8] by using the fillers forming composites with PANI. The increase in electrical conductivity in polyaniline has also been reported [6] for PANI/graphite nano-composites prepared as pellets and films.

Over the past two decades, interest in polyaniline has increased significantly as a conducting polymer and has shifted from others such as polypyrrole (PPY) because unlike redox doping exhibited by conducting polymers, polyaniline's protonic doping mechanism has advantages over redox doping in other conducting polymers. This has made it a competition to commercially available conducting polymers such as (3, 4-ethylenedioxythiophene) (PEDOT) systems in electronic applications [3] (Wagner, 2013). In the present work, an attempt has been made to synthesize and study ATR spectra of PANI and PANI-GRA Nano composites to see the change in the chemical structure of PANI due to GRA in the matrix of PANI.

2. THEORETICAL ASPECT OF ATR SPECTRA

In the FTIR spectra of a sample part of the infrared radiation is absorbed by the sample and some part of it transmitted. No two unique molecular structures produce the same infrared spectrum. It is therefore, the resulting infrared spectrum that indicates the uniqueness of the sample with absorption peaks which match with the frequency of vibrations between the bonds of the atoms comprising the material. Also the size of the peaks in the spectrum gives direct indication of the quantity of materials present. The bond positions in the IR spectrum are presented in wave numbers ($\bar{\nu}$) whose unit is the reciprocal centimeter (cm⁻¹) and ν is proportional to the energy of vibration.

$$\Delta E = h\nu = hc / \lambda = hc\bar{\nu}$$

Each absorption of radiation in the infrared region is quantized and usually appears as a spiky line. The analogy of a chemical bond with two atoms linked through a spring can be used to rationalize several features of the infrared spectroscopy [9]. The approximation to vibration frequency of a bond can be made by the application of Hooke's law. In Hooke's law, two atoms and their connecting bond are treated as a simple harmonic oscillator composed of two masses joined by a spring and frequency of vibration is stated as

$$\bar{\nu} \propto \sqrt{\text{(bond strength/mass)}}$$

$$\text{then } \bar{\nu} = (1/2\pi c) \sqrt{[K/(m_1 m_2 / m_1 + m_2)]} \quad (1)$$

Where m_1 and m_2 = masses of the two atoms, $\bar{\nu}$ = the vibrational frequency (cm⁻¹), c = velocity of light (cm/s), K = force constant of the bond (dyne/cm). The value of K is approximately 5×10^5 dyne/cm for single bonds and approximately two and three times this value for the double and triple bonds, respectively [9]. Taking $(m_1 m_2) / (m_1 + m_2) = \mu$, the reduced mass of the system, $\bar{\nu}$ can be written as

$$\bar{\nu} = (1/2\pi c) \sqrt{(K/\mu)} \quad (2)$$

Since according to equation (2) $\bar{\nu} \propto \sqrt{K}$, the vibrational frequency of a bond would increase with the increase in bond strength. As a result, it is expected that C=C and C=O stretching will have higher frequencies than C-C and C-O stretching, respectively.

Also $\bar{\nu} \propto \sqrt{1/\mu}$, the vibrational frequency of a bond would increase with the decrease in the reduced mass of the system. It implies that C-H and O-H stretching absorptions should appear at higher frequencies than C-C and C-O stretching frequencies. Similarly, O-H stretching should appear at higher frequency than O-C stretching. Further, as the stretching of the spring requires more energy than to bend it, the stretching absorption of a band always appear at higher energy than the bending absorption of the same band.

3. METHODOLOGY

3.1. Synthesis of Polyaniline (PANI)

5 ml of Aniline (0.054 mol) aniline monomer (C_6H_5NH) was added to 100 ml of 1M Sulphuric Acid (H_2SO_4), used as a dopant, in a 500 ml flat bottom measuring cylinder with a magnetic stirrer. 2 mg of Ferric Chloride ($FeCl_3$), used as a catalyst, was added to 100 ml of distilled water and the mixture added to the first mixture of Aniline and Sulphuric Acid and then continuously stirred using the magnetic stirrer. 100 ml of Hydrogen peroxide, used as an oxidant, was added to the mixture dropwise for about 20 minutes and the final mixture stirred continuously for 6 hours during which the colour changed from green to dark green indicating the formation of the half oxidized Polyaniline (PANI) called Emeraldine salt. The polyaniline salt was then left to stand for 24 hours during which the polyaniline salt was allowed to precipitate. The mixture was then filtered to obtain the dark green coloured polyaniline salt precipitate that was washed several times with distilled water and then finally with ethanol. The Polyaniline (PANI) thus obtained was put in a Petri dish and left to dry in air at room temperature for 24 hours. Again it was dried in oven for 6 hours at $80^{\circ}C$.

3.2. Synthesis of Polyaniline-Graphite (PANI-GRA) Composite

5 ml of Aniline (0.054 mol) was mixed with 100 ml of distilled water and 2 mg of Ferric Chloride ($FeCl_3$) was mixed with 100 ml of distilled water which was then added to the aniline solution and kept magnetically stirred. Again 5 mg of Graphite Nanoparticles was added to the mix and there after 100 ml of Hydrogen Peroxide (H_2O_2) was added drop-wise and was kept magnetically stirred. Finally, 100 ml of 1M Sulphuric Acid was added to this and kept magnetically stirred for about 1 hour during which the dark polyaniline/Graphite Nanocomposite started to precipitate. The mixture was then left to stand for 24 hours and the mixture was filtered to obtain the dark coloured powder form of the Polyaniline/Graphite Nanocomposite. After washing the filtrate several times with distilled water and then finally with ethanol, it was poured into a Petri Dish and left to dry in air at room temperature for 24 hours and also at $80^{\circ}C$ for 6 hours in an oven.

4. RESULTS AND DISCUSSION

The ATR spectra of the PANI and PANI-GRA composites' samples were taken using Perkin Elmer Spectroscopy Version 10.03.09 and the peaks that were observed at different frequencies are shown in Table 1.

Table 1

S.No Peak	PANI			PANI + GRA		
	X (cm^{-1})	Y (%T)		X (cm^{-1})	Y (%T)	
1	3844.01	80.02		3227.42	81.16	N-H stretching of Benzenoid ring
2	3743.77	80.54		3061.79	82.27	
3	3221.57	76.96	N-H stretching of Benzenoid ring	2112.49	90.33	

Synthesis and Study of ATR Spectra of Polyaniline/GRA Nanocomposites

4	2938.11	76.39		1567.8	65.9	C=N stretching modes of Quinoid rings
5	2351.75	78.72		1494.66	57.84	Are attributed to benzene ring, CH out of plane vibrations
6	1565.32	68.96	C=N stretching modes of Quinoid rings	1444.53	68.92	As a result of C-C aromatic ring stretching of the benzenoid diamine unit
7	1488.02	62.92	Are attributed to benzene ring, CH out of plane vibrations	1287.97	65.46	C-N stretching modes of benzenoid rings
8	1443.06	68.25	As a result of C-C aromatic ring stretching of the benzenoid diamine unit	1245.07	68.56	
9	1286.94	65.77	C-N stretching modes of benzenoid rings	1157.19	62.96	Combination modes of benzenoid and quinonoid unit
10	1147.30	62.43		822.48	67.84	C-H out of plane bonding in benzenoid ring
11	1075.67	63.50		756.26	65.51	
12	800.20	64.82		740.95	65.52	C-C, C-H bonding mode of aromatic ring
13	739.53	64.47		692.02	61.01	C-C, C-H bonding mode of aromatic ring
14	690.84	61.73		586.49	62.47	C-N-C bonding mode of aromatic ring
15	600.79	61.62		507.12	57.94	
16	505.51	57.88		493.28	57.66	
17	492.71	57.67		409.67	59.48	
18	406.38	58.91				

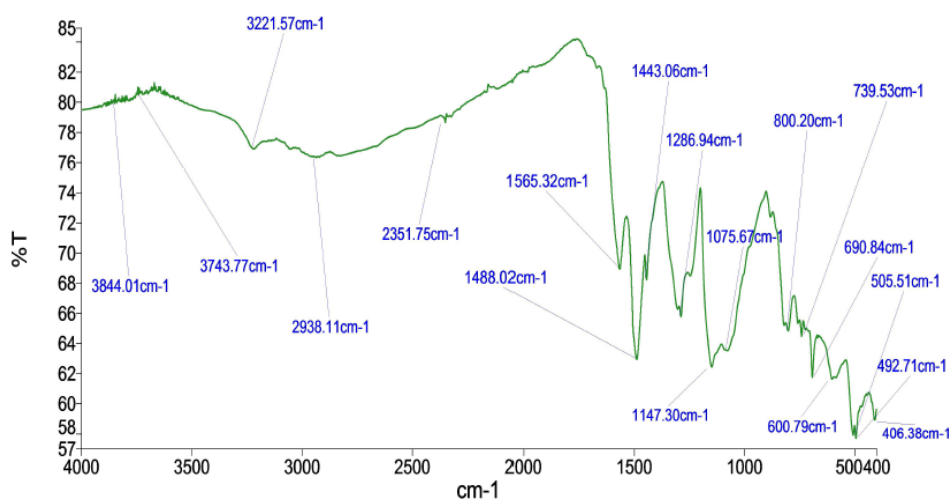


Figure 1 ATR Spectrum of PANI

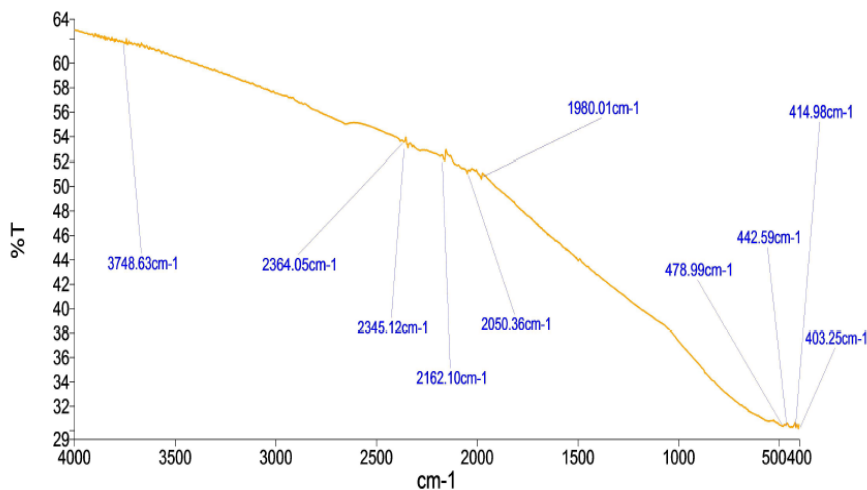


Figure 2 ATR Spectrum of GRA

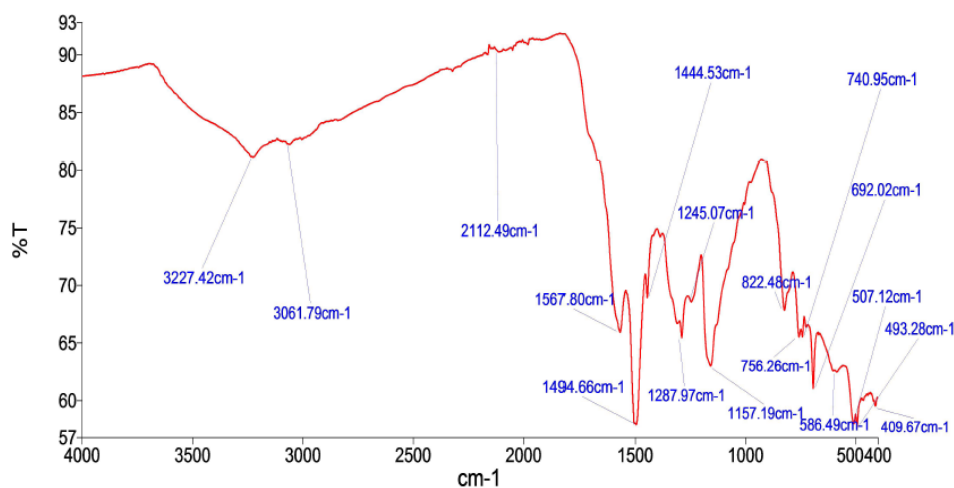


Figure 3 ATR Spectrum of PANI/GRA Composite

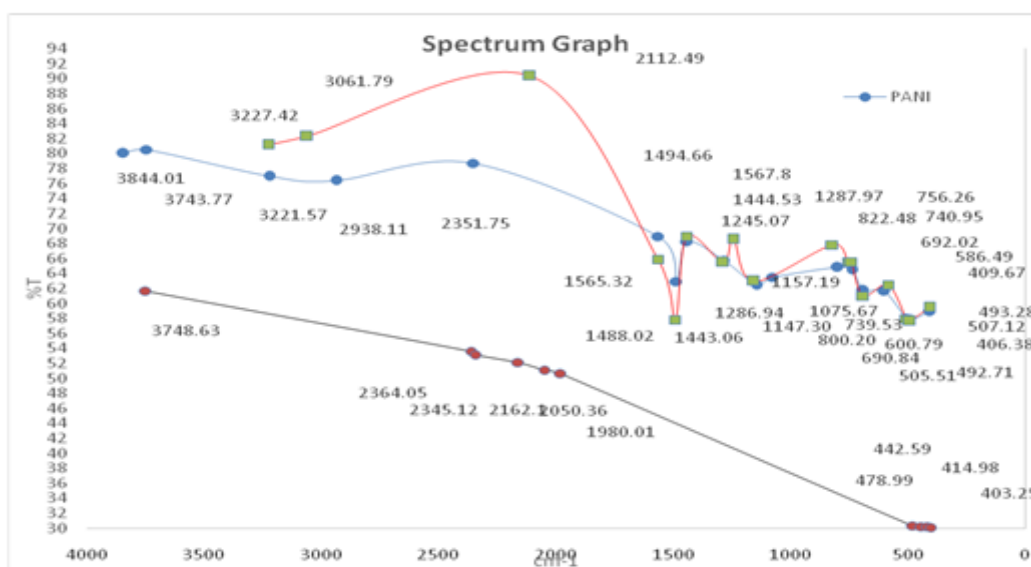


Figure 4 ATR Spectra of GRA, PANI and PANI/GRA Composite

In ATR spectra (Figures 1 and 3), the peaks at 1565.32 and 1567.8 cm^{-1} for PANI and PANI-GRA respectively are arising from C=N and C=C stretching vibration of the quinoid diimine unit (N=Q=N) [10, 11] while the 1443.06 and 1444.53 cm^{-1} wave number are as a result of C-C aromatic ring stretching of the benzenoid diamine unit [11, 12] for PANI and PANI-GRA composite respectively. Also the peaks at 1286.94 cm^{-1} and 1287.97 cm^{-1} are coming from C-N stretchings vibration in a polaron structure and that at 1147.30 cm^{-1} is assigned to aromatic C-H in plane bending [10, 12]. The peak at 822.48 cm^{-1} in PANI-GRA is as a result of C-H out of plane bending vibrations. The peaks at 412.08 cm^{-1} is coming from free oxihydroxides in the sample.

5. CONCLUSION

The attenuated total reflectance (ATR) spectra of samples as shown in Figs. 1 – 4 clearly demonstrate specific stretching vibrations in the PANI and PANI-GRA Nano composites. Also the deviation in transmittance in the PANI-GRA composite from PANI evidently illustrate the presence of GRA in the PANI matrix. This provides indication that the incorporation of GRA in the matrix of PANI will be very useful for the improvement of physicochemical properties of PANI.

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