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Synthesis and Characterization of Nanosized Graphene and Conductive
Polymers (Polyaniline) using some Ionic Liquids and Conventional
Solvents

By

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A thesis submitted in fulfillment of the requirements for the Master's
degree in Chemistry

In the Faculty of Agriculture, Science and Technology

(Department of Chemistry)

North-West University: Mafikeng Campus

B.Sc. Honours Chemistry (North-West University, South Africa)

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2013



M060072495

DECLARATION

I **Keolebogile Revelation Sebogodi** declare that this project which is submitted in fulfillment of the requirements for the degree of Master of Science in Chemistry (M.Sc.) at North West University, Mafikeng Campus has not been previously submitted for a degree at this university or any other university. The following research was compiled, collated and written by me. All the quotations are indicated by appropriate punctuation marks. Sources of my information are acknowledged in the reference pages.

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DEDICATION

To My Lovely Family... ..

My Father and Mother

My Sisters and Aunt

My Nephews and Nieces

ACKNOWLEDGEMENTS

First of all, I sincerely would like to thank my supervisor and co-supervisor Dr M.J. Klink and Prof. E. Ebenso respectively for their guidance, kindness and encouragement throughout this study. It has been a great experience to learn from them through the many discussions on chemistry and research and I am so grateful for their patience and trust.

My sincere thanks to all of my friends who shared my misery; they were a great support to me.

I deeply appreciate the North-West University (Mafikeng Campus) that embraced me as one of its students, and the South African National Research Foundation (NRF) for its financial assistance towards my studies.

Finally I feel indebted to every member of my great family especially my father, mother, and sisters without whom I would never be able to finish this degree.

Above all and before everything I am grateful to God for everything he gave me.

ABSTRACT

The graphene/polyaniline nanocomposites were synthesized in four different imidazolium based ionic liquids (1-butyl-2,3-dimethylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate, and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide) as well as in five organic conventional solvents (toluene, acetone, tetrahydrofuran, dimethylsulphoxide, and dimethylchloride) . Polyaniline was crafted on the surface of graphene oxide resulting in graphene oxide/polyaniline nanocomposites which were later reduced into graphene/polyaniline nanocomposites.

The graphene/polyaniline composites were characterized using Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FT-IR), Ultraviolet Spectroscopy (UV-Vis), X-Ray Diffractometry (XRD) and Thermogravimetric analysis (TGA). The SEM micrographs of composites synthesized in ionic liquids showed that the Polyaniline (PANI) nanofibers were nucleated and agglomerated in between the graphene sheets, while the PANI in composites synthesized in organic liquids formed slippery flakes in between the graphene (GR) sheets. The XRD distinctively identified the crystalline structures for GR/PANI nanocomposites synthesized in both ionic liquids and conventional solvents. The crystalline sizes ranged between 89-950 nm and 29-250 nm for composites synthesized in ionic liquids and organic solvents respectively. The FTIR and UV-Vis results shown that graphene was incorporated into the graphene/polyaniline nanocomposite structures. EDS and TGA depict that the graphene/polyaniline nanocomposites synthesized in the presence of ionic liquids have similar properties to those synthesized in organic solvents. Hence, this method could be employed to produce graphene based conducting polymer nanocomposites as a measure of producing materials in environmentally benign conditions.

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CHAPTER 1

INTRODUCTION

1.1. BACKGROUND

Material science has been part of our lives ever since the ancient stone, bronze, iron, steel, and silicon ages^[1-3]. The knowledge has improved our lives through the design and creation of new materials because the modern era lifestyle requires or rather really depends on, material that is of a high degree of sophistication^[2,3]. This sophisticated material is used in technology that adds convenience to our lives, thus the properties of materials should be improved and the only way to accomplish that is through imaginative molecular design and synthesis of new materials^[1]. The challenges of designing and creating new, reproducible, and diverse materials include the consumer market, demands to lifestyle improvement^[2], and limitations of environmental protection and public safety^[3].

In chemistry, material science seeks to understand the relationship between the constituents of materials such as atoms, ions, or molecules, and its overall bulk physical and structural properties^[2]. This simply means that it studies the structure and properties of existing materials with a goal of synthesizing and characterizing new materials with enhanced properties, and ultimately predicting the structures and properties of not yet made materials using advanced computational techniques.

While the study of materials was evolving, it was discovered that conjugated organic polymers which were at that time only thought of as insulators, could be made conductive^[4-6]. This breakthrough was made in 1977 when Shirakawa et.al^[4] synthesized and doped polyacetylene (PA) with a halogen. These conductive polymers were thereafter called “synthetic metals” because they have the characteristic resemblance of metals^[5]. Ever since then, more and more scientists have been focusing on understanding the in chemical structure and electronic mechanism, designing polymerization techniques, as well as developing physical and chemical modification methods for making more processable conducting organic polymers^[5,6]. Due to

their electronic transport, specific heat capacity, and mechanical properties, these polymers have a wide spectrum of applications such as sensors, light emitting diodes, electrochromic displays, energy storage devices and medicinal usage^[5].

Material science employed the concept of harnessing the properties of materials through hybridization^[1,3,5]. The field of polymer-based composites has in this regard been studied throughout the years because of their fascinating chemical structures, doping/dedoping chemistry, ease of synthesis, recyclability, and properties. These polymers have been hybridized with a variety of materials such as metals and carbon compounds, as well as with each other, and the composites/hybrids have shown spectacular properties.

New discoveries were made, nanoscaled materials were discovered, and these were also incorporated into polymers and their nanohybrids, which drew a huge amount of interest because of their outstanding optical, electrical, mechanical, and thermal properties^[7-10]. These properties are due to the fact that the nanoparticles have large surface area to volume ratios as compared to their macro- and micro-scale counterparts.

Composites based on polymers and carbon nanotubes have been studied extensively,^[11-13] but limitations came from the difficulty of dispersing carbon nanofillers on polymer matrixes, and because they are expensive^[7,14-16]. In 2004, the limitations encountered on carbon nanostructures were answered through the discovery of graphene by Geim and Novselov^[15,17]. Graphene has attracted more attention than carbon nanotubes because of its outstanding mechanical, electronic, and electrical properties^[17], low cost (graphene is synthesized from naturally occurring graphite) and lastly because of its surface area availability to the polymer matrixes^[18]. Graphene/polymer nanocomposites synthesis is exponentially increasing and they offer light-weight alternatives to carbon nanotubes and polymer nanocomposites.

1.2. PROBLEM STATEMENT

The rate of growth of technology is a global issue because it has to satisfy both personal demand and the consumer market, and hence there is a need of finding materials which are cheap and advancing these materials. This means that technology could reach unlimited achievements

through elevated rates of research and production of new, reproducible materials. Graphene based materials including composites show better properties (e.g. light weight) than silicon but due to the chemical oxidation which is involved during their synthesis, they contain oxygen defects and dispersing agents and as a result their electroanalytical applications (e.g. manufacturing of high performance electroanalytical sensors) are limited. Thus there is a need to be continuously seek methods of making technology fast and interesting by trying to solve the problems which seem to be obstacles that limit the applicability of materials

1.3. AIM OF THE STUDY

It is of great advantage that ionic liquids were invented and were seen as the promising solvents for the future because they are not only green but their introduction to materials tends to improve the material's properties giving it a huge application spectrum. For an example, Guo et.al^[19] showed that ionic liquid/graphene modified glassy carbon electrode displayed higher current signals for trinitrotoluene than glassy carbon electrode alone. Zhou and his colleagues^[20] investigated the synthesis of graphene/polyaniline (GR/PANI) nanocomposite nanosheets mediated by polymeric ionic liquids, but other than that the GR/PANI has not yet been thoroughly explored.

The aim of this study is to determine the effect of four different imidazolium based ionic liquids (1-butyl-2,3-dimethylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate, and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide), on the graphene/polyaniline nanocomposites prepared by in situ method in comparison with conventional solvents (toluene, acetone, tetrahydrofuran, dimethyl sulphoxide, and dimethyl chloride).

1.4. OBJECTIVES

The main objectives of this study are:

- (i) Preparation of nanostructure graphene/Polyaniline composites in the presence of some ionic liquids using in situ method.
- (ii) Preparation of nanostructure graphene/polyaniline composites in the presence of some conventional solvents.
- (iii) Physico-chemical characterization of these nanostructure graphene/polyaniline nanocomposites in ionic liquids and conventional solvents using different characterization methods (scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDAX), thermogravimmetric analysis (TGA), fourier transform infrared spectroscopy (FTIR), x-ray diffractometer (XRD) and ultra-violet visible spectroscopy (UV-Vis)) .

CHAPTER 2

LITERATURE REVIEW



2.1. INTRODUCTION

The words nanoscience and nanotechnology are a combination of the word nano from Greek “nanos”, or Latin “nanus”, meaning dwarf, and the word science or technology nano refers to the 10^{-9} power, or one billionth. Nanoscience is the study of atoms, molecules, and objects whose size is on the nanometer scale (1-100 nm)^[21,22]. It is very diverse, meaning that it ranges from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to investigating whether we can directly control matter on an atomic scale. Nanotechnology can be defined as the manipulation of matter on a nanometer scale to produce and develop materials, structures, and devices with new or vastly different properties^[23].

Nanoscience and nanotechnology are not really new but are rather the developments or extensions of pre-existing conventional sciences and technologies in the sense that they only modify conventional inventions. Thus they bring in the concept of material reconstruction, since micro-materials are now being reconstructed to form nanomaterials which offer exotic properties such as large surface areas, high physical strength, chemical reactivity, magnetism, and optical effects. Nanoparticles such as carbon nanotubes, metal nanoparticles, conducting polymer nanotubes/wires/belts, are of vital importance in research and have applications in electronics, medicine and construction^[5,21-24].

2.2. DISCOVERY OF CONDUCTING POLYMERS

Materials can be divided into three types according to their ability to conduct electricity; namely insulators, semiconductors, and superconductors^[25]. Depending upon the oxidation/doping state of a material, semiconductors have conductivity between 10^{-4} - 10^{-1} S/cm while that of metals/superconductors is larger than 10^3 S/cm^[5]. Organic polymers are generally classified as

semiconductors even though there are some which have similar conductivity to metals. The following table compares physical properties of conducting polymers, metals and insulators^[25].

Table 2.1: Comparison of physical properties of conducting polymers, metals and insulators^[25]

PROPERTY	CONDUCTING POLYMERS	METALS	INSULATORS
Electrical conductivity (S/cm)	10^{-1} - 10^3	10^{-4} - 10^6	10^{-20} - 10^{-12}
Carriers	Electrons of conjugated double bonds	Valence electrons of half-filled band	—
Concentration of carriers per cm^3	10^{12} - 10^{19}	10^{22} - 10^{23}	—
Effect of purity	Impurities of 0.1-1% change conductivity by 2-3 orders of magnitude	Effect comparatively slight	Strong effect
Magnetic properties	paramagnetic	Ferro and diamagnetic	Diamagnetic

Previously, organic polymers were only thought of as being insulators, until it was discovered otherwise around the 1970s^[26,27]. In order for them to be conductive they have to resemble a metal, thus the electrons in the polymer lattice should be delocalized^[25]. The polymer becomes highly conductive when an electron is removed from the valence band (*p*-doping) or added to the conduction band (*n*-doping). This doping process creates a hole which is the driving force behind the electron movement^[5].

The breakthrough in making conducting polymers came through as a mistake, when a student in Shirakawa's laboratory was attempting to synthesize polyacetylene and instead of a black powder, a silvery thin film was produced. This aroused Shirakawa's curiosity to know the motive behind the silvery film. After some investigations, he found that there was 1 000 times more amount of the Ziegler-Natta ($\text{Ti}(\text{O}-\text{N-But})_4\text{-Et}_3\text{Al}$) catalyst and that it was semiconducting^[5,28]. The silver colored *trans* isomer was formed at temperatures higher than 150 °C while the copper colored *cis* isomer was formed at temperatures lower than 78 °C^[5]. Thermodynamic studies showed that at room temperature the *cis* isomer is thermodynamically less stable than the *trans* isomer, that is *trans*-PA has room temperature conductivity $\alpha_{273\text{k}}=4.4\times10^{-5} \Omega^{-1} \text{ cm}^{-1}$ while *cis*-PA has $\alpha_{273\text{k}} = 1.7\times10^{-9} \Omega^{-1} \text{ cm}^{-1}$ ^[26]

At that same time, Heeger and MacDiarmid were conducting a study concerning the conductivity of polysulfur nitride $(\text{SN})_x$ and they found that its conductivity tends to increase when doped with halogens (e.g. bromine)^[5,28]. After MacDiarmid saw Shirakawa's work, he invited him to his laboratory and because polysulfur nitride and PA have one thing in common (covalent bonding) they decided to add a halogen to PA. When they measured the conductivity of halogen doped polyacetylene, they found that its conductivity was ten million (10^7) higher than in the undoped PA. This led to the joint publication between Heeger, MacDiarmid, and Shirakawa of "Synthesis of electrically conducting polymers: halogen derivatives of polyacetylene"^[4].

Since then it has been found that various organic polymers and their derivatives show enhanced electrical properties when doped with reducing agents (anions). This majestic discovery led to the studies that concern the understanding of conducting polymers, chemical structure and conducting mechanism, designing polymerization techniques as well as developing physical and/or chemical modification methods for making more processable conducting polymers^[5]. Figure 2.1. represents different conducting polymers^[25].

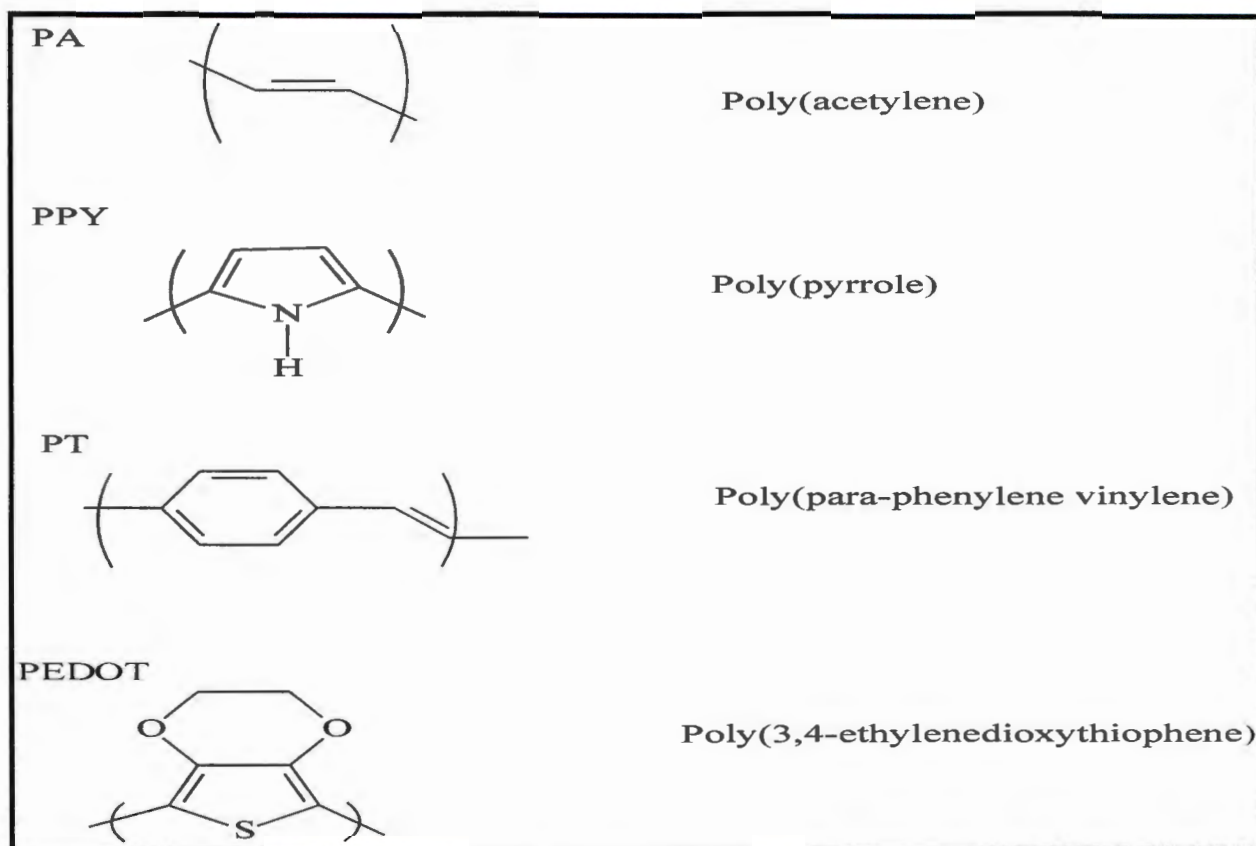


Figure 2.1: Some well-studied conductive polymers^[25]

2.3. DOPING CONCEPT

Conjugation as a primary requirement for polymer conductivity could be disadvantageous because it could cause polymers to be insoluble and to have poor mechanical properties, and thus limit or restrict their application in technology. Since the conductivity of polymers is achieved through doping, we should be aware that doping in terms of organic polymers is not necessarily the same as in inorganic semiconductors. Thus the differences are:^[5]

- Doping in organic polymers involves oxidation (*p*-doping) or reduction (*n*-doping) processes while doping in inorganic semiconductors involves atom replacement;
- Reduction of organic polymers could be accompanied by incorporation of a counter-ion into the backbone of the polymer chain, meaning that cations and anions are incorporated during *p*- and *n*-doping respectively. For example, when doping PA with iodine during

the oxidation process, the iodine molecule gains an electron (and becomes I_3^-) from the polymer PA chain, leaving the polymer positively charged. Thus the polymer now has now the counter-ion incorporated into its structure. This is not encountered in inorganic semiconductors. This doping can be achieved by various methods such as chemical, electrochemical, charge injection, and photo doping processes. The other kind of doping known as proton doping was discovered in polyaniline; this does not change the number of electrons associated with the polymer chain.

- As said above, electrical properties of conducting polymers can be changed from insulating to conducting form and the reverse could be applied to achieve the initial state in a dedoping process which is not possible in inorganic semiconductors. Changing the doping degree allows the conducting polymers to cover the whole insulator-semiconductor-metal region at room temperature, as shown in figure 2.2.^[5]

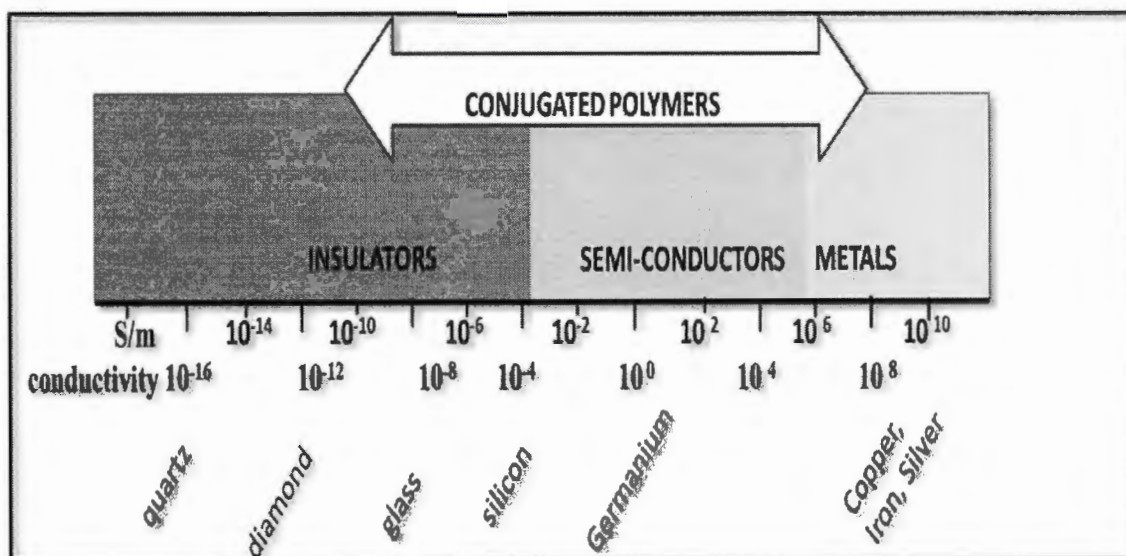


Figure 2.2: Conductivity of conducting polymers can cover the whole insulator-semiconductor region by simply changing the doping degree^[5]

- Conducting polymers can attain as high as 50% doping degree while inorganic semiconductors have very low doping degree. Thus there is higher electron density in conducting polymers than in inorganic semiconductors, but because polymers have poor crystallinity and defects, they have low mobility of charge carriers.

Table 2.2: Summary of differences between organic polymer and inorganic semiconductor doping

ORGANIC POLYMERS	INORGANIC SEMICONDUCTORS
Doping involves redox i.e. <i>n</i> -and <i>p</i> -type	Doping involves atom replacement
There is counter-ion incorporation	No counter-ions involved
There is doping/dedoping process	Only doping takes place
High doping degree	Low doping degree

2.4. CHARGE STORAGE



The band theory is used to explain the method of conduction in a polymer. This means that the ideal condition for electricity conduction is the formation of half-filled or unfilled electronic bands (i.e. valence and conduction bands). The intrinsic electrical properties of a polymer are determined by the width of the band gap between the two electronic bands. It was found that alternating (long and short) bonds lower the energy of the conducting organic polymer by introducing a band width of 1.5eV, making it a high energy gap semiconductor, i.e. making it to be intrinsically insulating^[28].

This band theory was previously used to explain the conduction in organic polymers simply because it was assumed that the mechanism of charge carrier generation (doping) in these polymers is the same as in inorganic semiconductors. On the contrary, it was found that organic polymers have conduction which has nothing to do with either the valence or conduction bands. It was rather revealed that conductivity is due to spinless charge carriers^[5,28].

The polymer stores charge by either losing an electron from one of the electronic bands or by localizing it over a small section of the chain. Charge localization costs the polymer some energy because it causes a local distortion (relaxation) due to the change in geometry, which in turn lowers the ionization energy of the polymer and makes it to have high electron affinity (the ability to accommodate newly formed charges). The localization of charge increases the energy

of the polymer by small amounts as compared with charge delocalization, and thus it is more preferred. The same charge storage mechanism occurs for a reductive process^[28].

Degenerate polymers (polymers with *cis* and *trans* isomers) have a charge storage mechanism which is slightly different from those of non-degenerate ones in the sense that the two isomers have exactly the same amount of energy. Due to their degeneracy, the charged cations (bipolarons) can freely separate because they are not bound to each other by higher energy configurations. This process of charge separation does not cause any sort of energy distortion. As the charges separate, they form a domain wall and move towards opposite ends of the chain. These chain ends would at the end be identical and have an equal amount of energy. The separated charged species are termed solitons (spinless) and could sometimes be neutral (1/2 spins)^[5,28].

The neutral solitons occur when a polymer has an odd number of carbon atoms. That is, there will be an unpaired π electron and a radical (which are equivalent to a soliton). The charge density of this neutral soliton becomes delocalized over several units of $-\text{CH}$, giving a soliton width. The band structure of the degenerate polymer consists of empty, half, and doubly filled bands i.e. they are formed by positively, neutral, and negatively charged solitons^[5,28].

Non-degenerate conducting polymers use polarons and bipolarons as charge carriers. During oxidative doping a free radical and a spinless positive charge are produced by removing an electron from the polymer backbone. The positive charge and the radical could be coupled to each other via their local resonance to form a polaron. Upon further oxidation the free radical of the polaron is removed and thus forms a bipolaron which is a spinless defect with a lower energy than the two distinct polarons^[5,28].

Intrinsically conducting polymers (ICPs) are an exciting class of materials which are based on heterocyclic compounds^[29,30,31]. These polymers include polyaniline (PANI), polypyrrole (PPY) and polythiophene (PTh). When compared to the polyacetylene family, the ICPs are non-degenerate and environmentally stable; and their structural changeability allows the modification of both their electrochemical and electronic properties by a simple manipulation of the monomer structure. The ICPs have the advantage of combining the high conductivities of pure metals with the processability, corrosion resistance and low density of polymers and therefore could be used in a variety of application fields. Among all these polymers, PANI is the most documented

because of its magnificent properties such as high electrical conductivity, unique reduction/oxidation ability, applicability, ease of synthesis, low cost and environmental and aqueous stability^[32-39].

2.5. POLYANILINE

The first polyaniline was synthesized in 1835 and it was known as Aniline black. It was produced via an electrochemical polymerization and unfortunately its electrical conductivity was not measured at that time otherwise it might had been the first conductive polymer to be discovered^[5,28,33]. Much interest in PANI studies is focused in developing physical and /or chemical modification methods in order to make a more processable PANI, understanding electronic conduction mechanisms and chemical structure, as well as designing polymerization techniques^[32].

2.5.1. MOLECULAR STRUCTURE OF POLYANILINE

PANI has three major molecular structures which differ according to their degree of oxidation. Carbon-13 Nuclear Magnetic Resonance (¹³C-NMR) spectra analysis led to the proposal of the molecular formula of PANI in which the results suggested that it has alternating imine and amine repeating units^[5,37]. Because PANI exhibited different colors which had to be accounted for, it was then assumed that it must have two other forms where one is fully reduced and the other one is fully oxidized. Thus the forms of PANI are: the yellow leucoemeraldine base with amine monomers, a blue emeraldine base with alternating amine and imine monomers and a purple pernigraniline with imine monomers (figure 2.3)^[5,40].

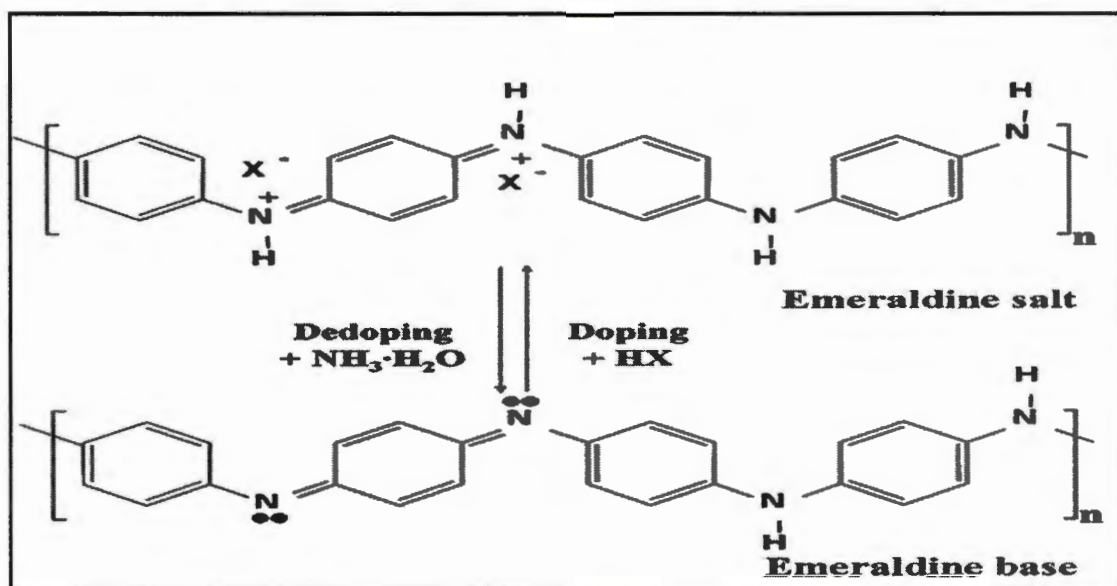


Figure 2.4: The doping/dedoping reversibility of PANI using an acid and a base^[32,40]

Proton doping should not be confused with redox doping. The former does not involve changing the number of electrons with the backbone of the polymer while later redox doping gives rise to the three molecular structures of PANI by either removing or adding the electrons to the base^[5,32,41].

Wan and Yang^[42] used ultra-violet visible spectral analysis to confirm MacDiarmid's proposal of the occurrence of proton doping only at the imine links of the emeraldine base. The following results were observed: the emeraldine base showed two peaks at 325 and 630nm which are due to excitation of amine and imine respectively, but the emeraldine salt exhibited peaks at 325 and 950nm which are due to excitation of the amine and proton doped imine.

2.5.2. SYNTHESIS OF POLYANILINE

Aniline polymerization can be performed at room temperature at pH of 0.0-2.0 in the presence of acids such as hydrochloric (HCl), hydrofluoric (HF), perchloric (HClO₄), acetic (CH₃COOH), trichloroacetic (Cl₃CCOOH) etc., which can also act as doping agents for the resulting polymer and can also proceed in neutral and alkali media^[43]. In an acidic medium, oxidative chemical polymerization of aniline could be performed using oxidizing reagents such as hydrogen peroxide (H₂O₂), copper(II)salts, potassium iodate (KIO₃), potassium dichromate (K₂Cr₂O₇),

ferric chloride (FeCl_3) and potassium permanganate (KMnO_4)^[5,37,39]. This is achieved by either electrochemical or chemical oxidative polymerization techniques. Huang *et al*^[44] reported a less commonly used mechano-chemical polymerization technique which involves inducing a reaction between an aniline salt (e.g. aniline /CSA salt) and an oxidant by ball milling followed by high speed spinning in a planetary micro-mill. The end product was found to be PANI in its conductive form (emeraldine salt). These polymerization methods have been proven to be producing micro-(structured/scaled) PANI which is highly agglomerated or aggregated, and that the chemical polymerization methods produce the polymer in larger yield quantities than those produced by electrochemical methods^[5,32].

In the synthesis of nanoscaled materials, the emphasis has been on producing structures with controlled morphology and size^[45] and therefore to achieve that, nano-PANI has been synthesized using different techniques such as chemical, physical and electro-chemical polymerization methods^[46].

2.5.2.1. CHEMICAL SYNTHESIS OF NANOSTRUCTURED POLYANILINE

The chemical route has been adapted from the traditional way of polymerizing aniline, and could be divided into template and template-free synthetic methods.

2.5.2.1.1. Template Methods



Template methods are divided into two types which are the physical/hard and chemical/soft template methods depending on whether the template is soluble or not in the reaction medium^[35,38].

2.5.2.1.2. Soft template methods

The soft template method is an approach which is used to synthesize conducting polymer nanostructures and it has been previously referred to as the template-free or self-assembly method (in a way that meant no hard or physical template is used). This method entails fabrication of a polymer in the presence of the structure directing molecules. This is based on

self-assembly mechanisms which are due to hydrogen bonding, Van der Waals forces, π - π stacking, and electrostatic interactions as driving forces for creation of well-defined structures at a molecular level^[5,46].

Until now seeding, surface micelles, enzymatic, micellar polymerization, etc. have been used as soft templates for one-dimensional nanostructured polymer production. These methods are cheaper and much simpler than hard template methods because there is no hard template involved and therefore no tedious post-processing required^[5,46,47]. The reaction conditions, such as the type of soft template and the aniline oxidant ratio, influence the type of nanostructure that will be formed. For example, ambient aniline concentrations favor nanotube or nanofiber formation while high aniline concentrations favor granular PANI formation^[35].

Seed polymerization is a synthetic approach which involves using a foreign material (seed) as a polymerization director. PANI nanostructures have been synthesized in the presence of different seeds such as PANI powder oligomers, carbon nanotubes, Au nanoparticles, and V₂O₅ nanofibers^[5,35]. Several factors such as monomer concentration, seed to solvent ratio, solvent, acid type and seed type affect the morphology of the produced polymer, but among these the monomer concentration and type of solvent are of most importance. Thus, the higher the monomer concentration the thicker the nanostructures, and the higher the seed solubility in the solvent the more aggregated the PANI is^[36].

Seed polymerization has the following advantages: (i) it is a cheap, one step approach which produces high quality yields, e.g. Zhang *et al*^[48] used 1-4mg seed to produce about 200g PANI nanofibers, (ii) the seed can also act as an oxidant, e.g. Zhang *et al*^[48] reported that chemical oxidative polymerization of aniline with APS as an oxidant produces anilinium peroxydisulphate ion clusters which act as in situ generated seeds and (iii) there are no post treatments required.

The enzymatic polymerization soft-template method is a simple, eco-friendly process which produces conducting polymers in large yields, and with controlled size distribution and morphology^[33]. This is a biocatalytic polymerization process which uses an enzyme such as a naturally occurring horse radish peroxidase (HRP) as a catalyst^[36,49]. Nakao *et al*^[50] and Nickel *et al*^[51] incubated the DNA templates in a solution of protonated aniline in order to align the protonated monomers along the DNA chains, followed by enzymatic polymerization which

occurred after the addition of hydrogen peroxide and HRP. This resulted in the formation of PANI nanowires which had better properties than the one prepared by oxidative chemical polymerization of aniline by APS. The disadvantages of this method are that it could be costly because it depends on the nature of the biomolecules, and the variation of reaction conditions could affect reproducibility^[49].

Micellar polymerization is one of the soft template methods in which micelles are used as the polymerization medium, and can also act as the dopant and as the stabilizing agent. This method is simple, cheap, and produces soluble and stable polymers^[49]. The morphologies of polymers could be controlled by simply changing the concentration and the nature of the surfactant/micelles. PANI nanostructures with varying morphologies such as those which look like rice grains, needles, and spheres have been produced^[52].

In a typical micellar synthesis of conducting polymers, there is protonation of the monomer in an acid and the attractive static interaction between the micelles (which are negatively charged) and the monomer (which is positively charged). The increased concentration (which is caused by the interaction between the micelle and the monomer) around the micelle causes the accelerated polymerization at the interface^[55]. DBSA has been used as a micelle and dopant to synthesize large quantities of PANI nanostructures which were 10 to 102 nm in diameter and had a spherical shape^[56]. The micellar synthesis suffers from the drawback that it is difficult to remove all the moisture in the polymer^[49].

2.5.2.1.3. Hard template methods

The hard template method depends on the existing nanostructure replication by either chemical or physical interactions. This method is used to synthesize nanotubes/wires with desirable length and diameter. This is achieved by synthesizing the polymer within the pores of the nanoporous template membrane, hence the replication of the existing nanostructure. Thus, the diameter of these pores ultimately determines the polymer's diameter^[5,36,46,47]. The material's length and thickness depend on the polymerization time^[5,41]. This technique employs both chemical and electrochemical polymerization methods which is of great importance for conducting polymer synthesis, because they could be synthesized using both the polymerization methods^[33,41,49]. The

disadvantage of the hard template method is that it requires post-treatments which aim at removing the template membrane. Thus, the template and the nanostructures could be separated by either dissolving the nanostructures in a suitable organic solvent or by dissolving the template itself, and this may alter the structure of the resulting material^[36,41,49]. Figure 2.5 shows different hard-template methods. What actually happens in this scheme is that: (a) a membrane which serves as a template which directs the formation of PANI nanostructures is inserted in a solution of an aniline monomer and after polymerization has been initiated by addition of APS, the polymers will be formed in the channels of the membrane. After the completion of polymerization, the membrane is removed; (b) a polymer could be polymerized on the surface of other nanofiber, and then the nanofiber is removed by either dissolving or depolymerizing it to obtain the nanotube, and (c) colloidal particles could also be used as a hard-template membrane to produce a 3-dimensional polymer, and also in this case the colloids are removed after polymerization of polymer monomers.

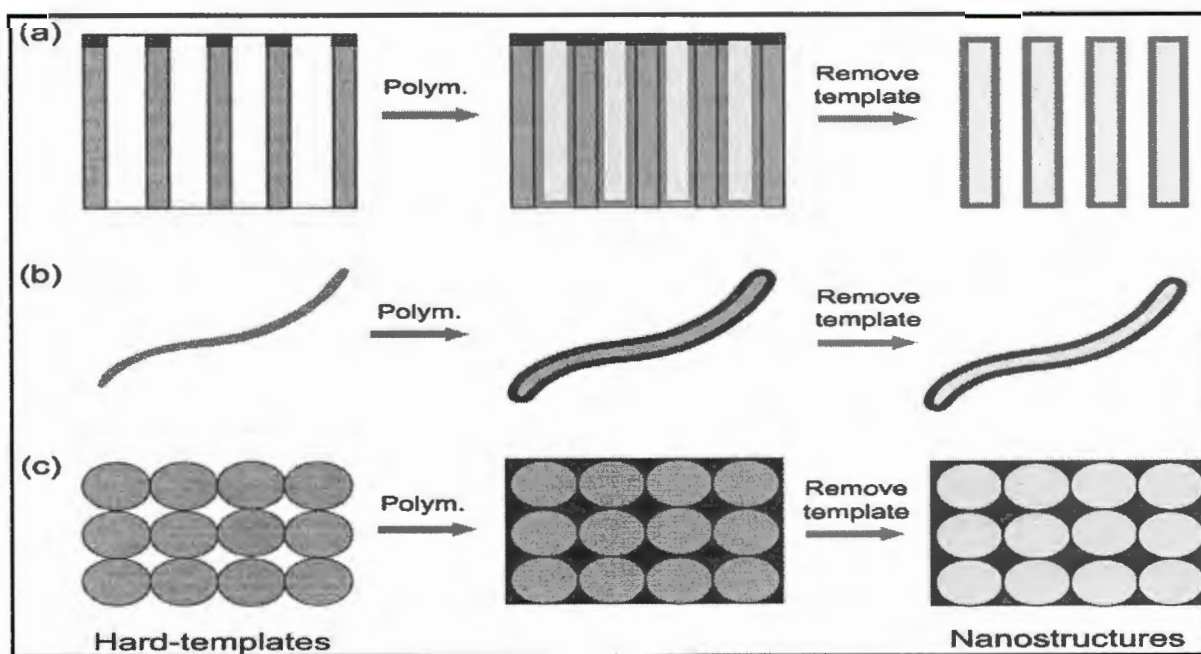


Figure 2.5: Schematic representation of the hard-template synthesis of conducting polymer nanostructures^[41].

The hard template chemical polymerization method requires the immersion of the template in the mixture of aqueous liquid and the monomer, followed by addition of the initiator. The capillary phenomenon of nanopores limits the entrance of the monomer and initiator into the inside of the

pores, but in the case of conducting polymers this problem is solved by the ionic characteristic found on the nanopore walls (anionic) and in the monomer (cationic)^[5,41,49].

The hard template electrochemical polymerization technique requires that the membrane surface should be coated with a metal film (the film resembles the working electrode in a traditional synthetic set-up). This is the surface on which the polymer would form. The chemically synthesized polymer length and thickness are determined by polymerization time while the length and thickness of the electrochemically synthesized polymer are determined by polymerization time together with current density and voltage applied^[5,41,49].

2.5.2.1.4. Template-Free Synthesis

Template-free polymerization techniques employ no template, either hard or soft. Some of the techniques used in this category are interfacial, rapid mixing, sonochemical, and radiolytic polymerization.

The interfacial polymerization is a polymerization technique in which two immiscible solvents are used, one solvent should contain a monomer while the other one contains an oxidant. During conventional chemical polymerization of aniline, the monomer and the oxidant react on the surface of the already formed PANI (because of slow addition of an oxidant into the monomer solution), and this creates a coarse, inhomogeneous nanofibrous polymer^[5,32,49]. This secondary growth is not encountered in an interfacial polymerization because PANI is hydrophilic and therefore immediately after the reaction it migrates to the aqueous phase, thus leading to the formation of pure homogeneous nanofibers at the interface^[34,41](figure 2.6). The diameter and uniformity of the fibers are affected by both the concentration of the acid and the acid itself. It was found that medium and weak acids form mixtures of particles and nanofibers at low and high concentrations and that low concentrations of strong acids form lower fractions of nanofibers. The advantages of this method are that the nanostructures produced have good processability because they are readily dispersed in water, they are uniform and they have the same sizes and morphology. The disadvantage is that this method is limited to the production of nanofibers and nanorods^[49].

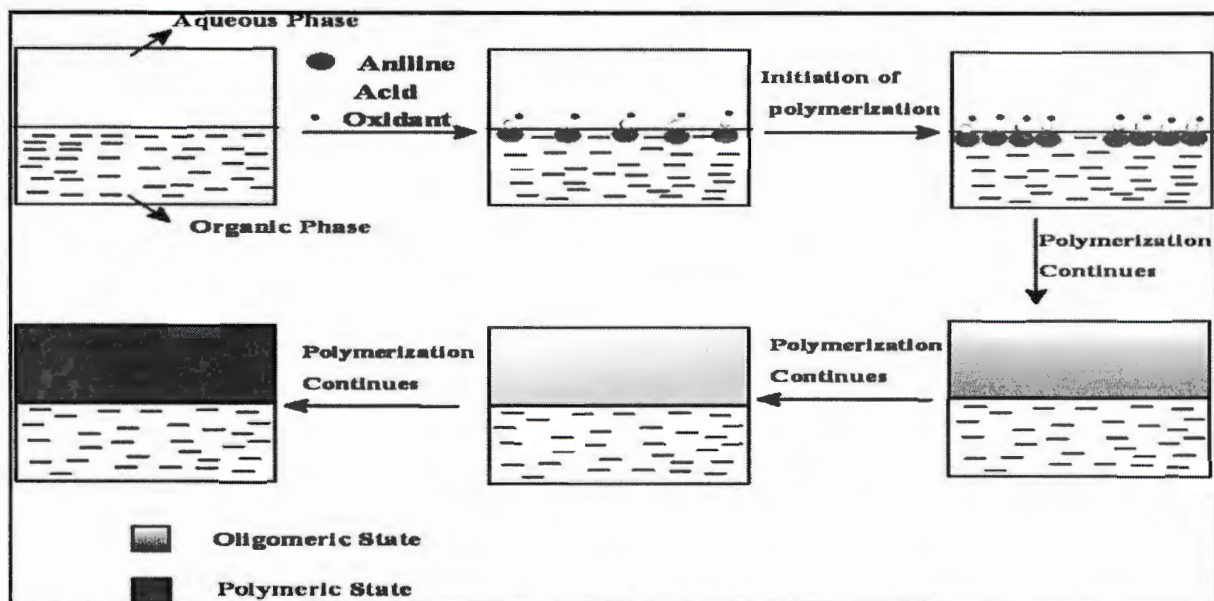


Figure 2.6: Schematic diagram for interfacial polymerization^[49].

Conventional chemical polymerization of aniline forms polyaniline nanofibers but because of the slow addition of an oxidant and vigorous stirring, these nanofibers suffer a lot from secondary growth/re-nucleation. This polymerization method could be used to produce nanofibrous PANI with no agglomerates by simply mixing the monomer and oxidant solutions rapidly so that the polymerization could occur at once^[32]. Li and Kaner^[54] reported in their paper “shape and aggregation control of nanoparticles: not shaken, not stirred” that nanostructures with controlled shapes and sizes could be synthesized by not using mechanical stirring (which is traditionally used to disrupt aggregates). This paper clearly shows that the stirring triggers aggregation.

Sonochemical polymerization is the synthetic procedure that is analogous to the conventional PANI synthesis but with the aid of ultrasonic irradiation^[35,36]. This method was used by Jing *et al.*^[55,56] to produce high quality PANI with high yields. If there is high monomer (aniline) and oxidant (APS) concentration in the synthesis of the conventional PANI, three possible competitive reactions may be taking place, which are: (i) ongoing primary nanofiber formation, (ii) the growth of primary nanofibers into uneven surfaced thick fibers, and (iii) further growth and agglomeration of thick fibers into irregular particles. The growth and agglomeration of thicker fibers which are experienced in the conventional synthesis of PANI is in this method effectively suppressed (by the ultrasonic irradiation)^[55]. The diameters of PANI fibers produced by this method using different oxidant to monomer ratios are equal but their lengths increase

with decreasing APS to aniline ratios^[56]. The advantage of this method is its scalability as compared to the rapid mixing and interfacial polymerization methods^[35,36].

The radiolytic polymerization procedure involves irradiating the mixture of monomer and oxidant solutions with high energy rays. Pillalamarri *et al*^[57] irradiated aqueous solutions of aniline, APS, and hydrochloric acid with gamma rays. They mixed 0.3M HCl, 0.1 M aniline in distilled water, and varying concentrations of APS which range between 0.002 to 0.1M and irradiated the mixture. Rod like structures with diameters of 250-500nm, and lengths of 5-10 μ m were observed in polymers formed in solutions which contained 0.050-0.1M aliquots of APS. The radiolysis was proved not to have affected the polymerization reaction strongly but it did affect the resulting PANI morphology, that is, when only an aqueous solution of monomer was irradiated PANI had spherical aggregates with diameters which were four to five times larger than that of unirradiated ones (which have 20-40 nm diameters). The hollow spheres with diameters between 50-100 nm were also observed in the irradiated PANI. The hollow aggregates tended to stick to and to link spheres which coalesced in an anisotropic fashion^[58].

2.5.2.2. PHYSICAL METHODS

2.5.2.2.1. Electro-spinning

The electro-spinning technique uses strong electrostatic forces to synthesize polymer fibers which are as long as 100m with diameters less than 100 nm. Generally a high electrical charge is applied between the polymer solution and the metallic collection screen (grounded collector), and at the critical point the charged jets are produced from the syringe tip (Taylor cone) (figure 2.7). During the jets way to the collection screen, they undergo electrically induced instabilities (whipping and or splitting motions which are initiated at the small bends in the fiber). These whipping motions tend to elongate the charge jets. The fibers are then collected on the collector^[46].

Electro-spinning is advantageous because it is used for production of long fiber and non-woven polymer meshes, and most importantly it ensures that no solvent is carried over to the final product, simply because the whipping and splitting motions are accompanied by rapid solvent evaporation. It is difficult to produce conducting polymers using this technique because the

process requires that the polymer should be highly viscous^[46]. This problem could be solved by dissolving a pre-synthesized polymer in a solvent with a low melting point^[58].

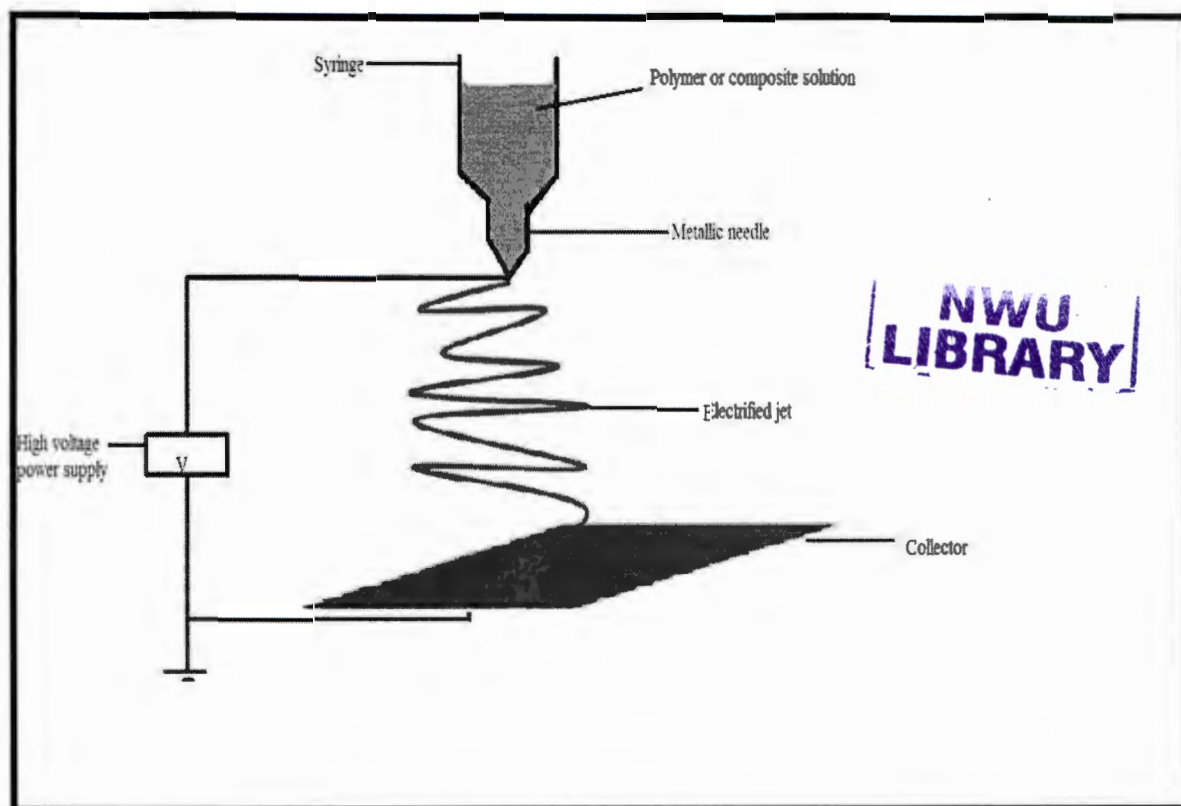


Figure 2.7: schematic representation of electro-spinning setup used for synthesis of polymers^[46]

This technique could also be used for fabricating conducting polymer nanocomposites. This means that the conducting polymers are coated on the surface of the template during the in-situ deposition polymerization process. This is then followed by the removal of the template^[46]. Diaz-de León^[58] blended PANI with polystyrene (PS) and polyethylene oxide (PEO) using the electrospinning technique and the results showed that the PS blended PANI had diameters which were less than 1000nm. This means that it is better to blend PANI with PS than with PEO because the smaller the diameter of the material the better the conductivity and properties. Another group synthesized the gelatin-PANI composite for the use in tissue engineering^[59].

2.5.2.3. ELECTROCHEMICAL METHODS

Nanostructured polyaniline could also be fabricated using the conventional electrochemical polymerization method. In this method aniline monomers undergo electrochemical oxidation at high positive electrode potential and form reactive radical species such as cation radicals. It is these radicals which trigger the polymerization process.

Electrochemical polymerization techniques could be used for fabrication of PANI with various morphologies such as nano-wires, fibers, and rods. These morphologies are dependent on experimental variables which include: the type of electrolyte used, monomer concentration, charge density, polymerization time and the electrode potential^[36,41].

Electrochemical methods have advantages over chemical oxidative methods. For instance they can easily to be controlled by simply changing the current passed through the counter and indicator electrodes, applied voltage, and polymerization time, small quantities of reagents are used, and the quantum of the product is limited by the size of the working electrode^[5,34,49]. Electrochemical polymerization can be divided into templateless^[60-62], template-assisted^[5,36], and molecular template-assisted syntheses^[63].

In template-less synthesis, the polymeric nanostructures are obtained by choosing the appropriate electrosynthetic conditions at a chemically inert electrode, for example PANI powder which adheres weakly on the surface of the electrode can be produced by applying a constant potential at the electrode^[60], and a thicker PANI film which adheres strongly to the electrode surface of the electrode can be obtained by simply polymerizing aniline between the predetermined potentials^[60-62].

In the electrochemical template assisted synthesis of nanostructured PANI (and other conducting polymers), the monomer is polymerized in the cavities, holes, or channels of the nanostructured electrode plate surface^[36]. The most popular nanostructured architectures are the alumina (aluminium oxide) and the track-etched polymer membrane^[5].

In molecular template-assisted synthesis, hard and soft templates influence the morphology of the resulting polymer, that is the adsorbate is used to modify the surface of the electrode and hence direct the electropolymerization to proceed in a template-like method^[62].

2.5.3. APPLICATIONS OF POLYANILINE

Polyaniline and all conducting polymer nanostructures display better properties than granular conducting polymers. These properties, which include high electrical conductivity, large specific surface area, and short path lengths, enable the nanosized polymers to be used in a spectrum of technological applications, such as sensors, energy storage devices, and field emission applications.

2.5.3.1. SENSORS

A sensor is an electronic device which is divided into optoelectronic and electrochemical devices. Conducting polymer (CP) sensors have been explored as chemical, optical and biosensors based on the unique reversible change in conductivity which results from the doping/dedoping processes displayed by these polymers^[5,6,34,46,]. Nanostructured conducting polymers have large surface areas and porosity and therefore respond faster than their conventional counterparts^[5,6]. Their porosity allows for better in and out diffusion of molecules, giving the nanostructures faster responses. The larger exposure surface and smaller sizes of fibers are attributed to the shorter response time; the smaller the diameter of the nanofiber the faster the diffusion^[49]. For example, it was found that the one dimensional polyaniline nanostructure responds twice as fast when exposed to chloroform, toluene, and triethylemine, as compared to bulk PANI^[47].

2.5.3.2. ENERGY STORAGE

Energy is one of the world's greatest challenges because humankind relies on it and without it life would probably end. The problem is that most of our energy is produced from nonrenewable sources such as fossil fuels which take centuries to form but could be depleted within a very a short period of time. During energy conversion from fossil fuels the combustion process leads to negative impacts on the environment. There is a need for "greener" and more efficient energy production, transmission, and utilization. Alternative and renewable energy sources such as nuclear power, solar energy and hydropower should be used. When energy is produced from

alternatives there is always a question of its storage. The answer could lie in the various possible energy storage systems that are available; these include super capacitors, fuel and photovoltaic cells, and rechargeable batteries, which need to be developed or advanced from time to time^[63].

Electrochemical studies showed that the CP nanostructures have high capacitance values which could be beneficial in the development of the next generation storage devices. Thus Virji *et al*^[6] and Zhang *et al*^[64] reported that PANI nanofibers have the capacitance value of 122 F/g which is far more than the one reported for conventional PANI which is 33 F/g and more symmetrical cycles due to their large available surface area. Kuila and his colleagues^[65] reported that the highly dense arrays of ordered and aligned polyaniline nanorods with a diameter of 10nm exhibit an electrochemical capacitance value of 3407 F/g.

2.5.3.3. TRANSPARENT COATINGS

Materials such as carbon black and transparent inorganic conductors (such as indium-tin oxide) have been researched for their use in coating systems. They showed some drawbacks such as^[66]:

- Carbon black→ it is impossible to achieve transparency and antistatic coatings using carbon black.
- Inorganic conductors→ their brittleness, poor long term performance, and the fact that they don't function well in all climates are disadvantages.

These drawbacks compelled scientists to find other materials which could be used in coating systems and they found that the intrinsically conductive polymers (ICPs) serve as better substitutes. PANI as the highly praised and appreciated ICP has been intensively studied for usage in coating. Its blend coatings are made-up by dispersing its powder in coating systems such as soft PVC, poly-(methylmetacrylate), phenol-formaldehyde resin. The pre-conditions of a 0.3-5 μ m coating with transparency of ~95% are that^[67]:

- the critical volume concentration at which sudden conductivity breakthrough must be ~1%, and
- the dispersed phase must be ~70nm.

The PANI blend coatings could also function as sensors and electrochomics.

2.5.3.4. CORROSION INHIBITOR

Corrosion is one of the processes that have been on earth ever since life began to exist on it. It is a destructive process, and it is necessary to find ways of inhibiting it. Several corrosion inhibitors exist.

The study of PANI as a corrosion inhibitor dates back to around 1985 when DeBerry^[68] electrodeposited it on pre-passivated steel and supposed that the pre-formed passive state on the metal surface was maintained by a PANI layer. Another group of scientists carried out studies using PANI as an inhibitor on various metal surfaces. They used PANI-paint blends and produced promising results^[69].

A study of interactions between metal surfaces and PANI coatings was undertaken and this led to the conclusion that the passivated metal surface (passivated e.g. iron dioxide) together with PANI coatings have a significant anti-corrosion effect^[70]. To date, several other studies concerned with PANI as a corrosion inhibitor are available and their results have been used to develop various commercially useful anti-corrosion products. The following are the requirements of making commercially attractive PANI coating blends^[66]:

- the PANI within the paint must be well dispersed,
- the PANI must be in its conductive form (emeraldine salt),
- the PANI coating must meet industrial requirements in terms of adhesion i.e. it has to adhere well on the metal surface,
- the paint must have metallic properties/character in order to ennoble the metal surface,
- coatings should offer chemical reactivity throughout the whole primer volume,
- both the primer and the complete coating system must be mechanically and chemically stable, and
- the coatings are designed for a specific application.

2.6. GRAPHENE

As the need for technology increases, the technological discoveries have become more important, hence nanoscience and nanotechnology were discovered.

In 1980, when Iijima was studying thermal vacuum deposited amorphous carbon films using electron microscope images, he discovered that the films had carbon nanocages also known as graphite onions^[71]. Another study concerning Iijima's findings was carried out in 1988 and it proposed that the carbon nanocages consisted of nested icosahedral fullerenes. These were made of pentagonal and hexagonal carbon rings^[72]. This discovery laid a foundation for carbon nanoscience.

Carbon nanoscience (carbon black and carbon nanotubes/wires) became the subject of research. It was super ceded by the study of graphene in 2004^[17]. Research on graphene has focused on its synthesis, structure, properties, spectroscopy and applications^[73] (figure 2.8).

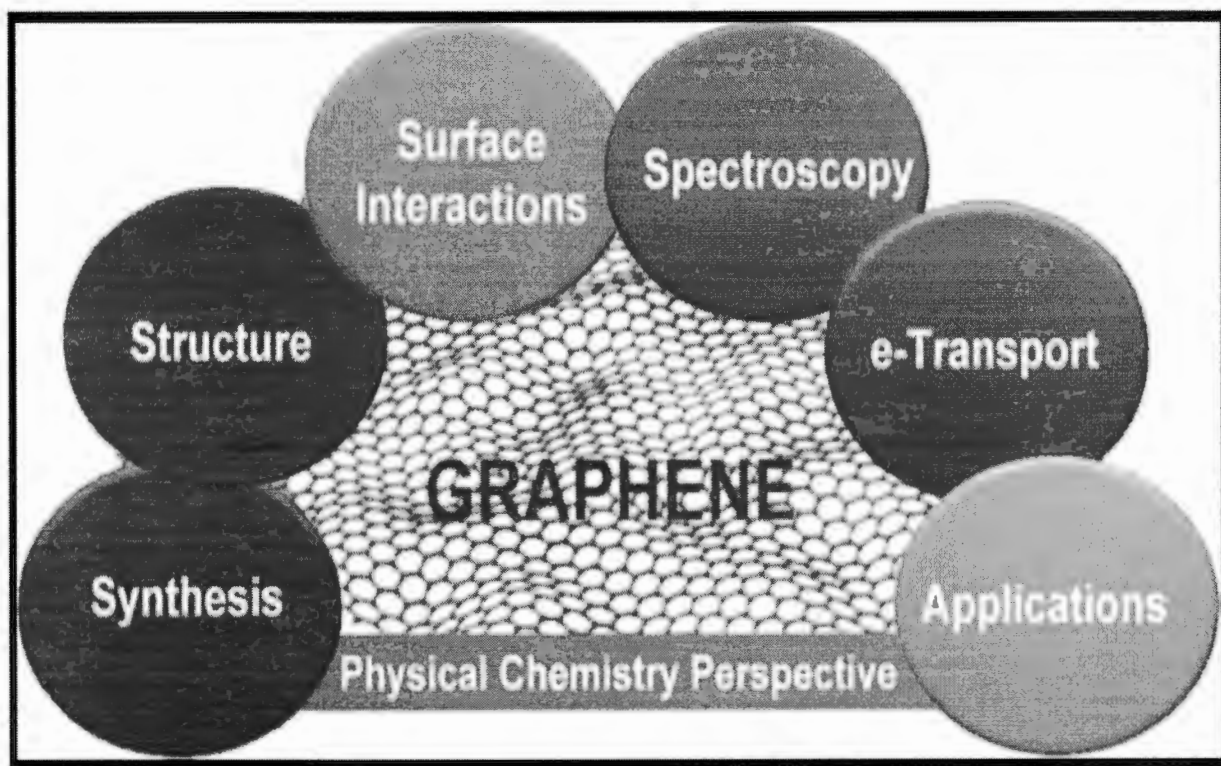


Figure 2.8: Fundamental information of graphene based materials through physical chemistry^[73]

2.6.1. TOWARDS GRAPHENE DISCOVERY AND HISTORY OF GRAPHENE

Graphene was discovered around 1900 and it was known as graphite layers. These findings were not given a lot of attention because it was believed that a free standing, stable two dimensional molecule could not exist and perhaps because the analytical instruments were not advanced enough at that time. Since the discovery of graphene in 2004, a lot of research has been focused on its synthesis and the understanding of its properties. After the synthesis of free standing graphene, it was then realized that if graphene was to be called graphite layers it would mean that it is a three dimensional lattice which would not allow it to take other forms or dimensionalities^[74].

The history of graphene is shown in the Table below.

Table 2.3: The history of graphene



YEARS	ACCOMPLISHMENT
1840-1958	Synthesis of graphite oxide ^[75-79] .
1962	Thermal and chemical reduction of graphite oxide ^[80,81] .
1968	Epitaxial synthesis of graphite monolayer on top of Pt (0001) ^[82]
1970	Monolayer graphite prepared by segregating carbon on the surface of Ni(100) ^[83-89] .
1975	Graphite monolayer prepared by subliming silicon from SiC ^[90] .
1986-1987	The term graphene was used to describe single sheets of graphite as one of the constituents of graphite intercalation compounds (GICS) ^[91] .
1999	Micromechanical exfoliation of graphite into lamellae consisting of multiple graphene layers ^[92,93] .
2004	Micromechanical cleavage (scotch tape technique) of graphite used to prepare graphene- this is when graphene was officially born ^[17,94] .

2.6.2. SYNTHESIS OF GRAPHENE

There are various ways of producing a single material, but the resulting compound may possess minor different features due to the preparation conditions (pH, temperature, pressure, etc.) under which the material was synthesized. The preparation routes may be disadvantageous and may limit the compound's application. Like any other nanoparticle, graphene can be synthesized employing the bottom-up and top-down synthetic preparation processes^[94,95].

2.6.2.1. BOTTOM-UP GRAPHENE

Bottom-up approaches use molecular assembly and a recognition concept to produce a compound, that is, the material is built from the bottom (atom-by-atom, cluster-by-cluster, and molecule-by-molecule) and less waste is encountered. Preparation methods such as chemical vapour deposition (CVD), arc discharge, epitaxial growth on silicon carbide (SiC) and unzipping of carbon nanotubes are used in bottom-up processes of graphene synthesis. Among all these methods, only the epitaxial growth on SiC and CVD are capable of producing graphene sheets with no structural defects and thus they are of more interest when coming to the fundamental studies (e.g. morphology) and electronic applications. Disadvantages of about the so produced graphene produced in way is that it cannot be used as a polymer filler or for making polymer nanohybrids^[95].

2.6.2.1.1. Thermal Chemical Vapour Deposition (TCVD)

This is a process used to produce high-purity and high performance graphene sheets on solid materials. In a typical TCVD process, the metal (Nickel-Ni) is exposed to hydrocarbon gases (usually methane-CH₄ gas) which segregate or decompose on the substrate surface to produce the desired deposit. In this process, carbon rearranges itself into graphene on the metal surface. The process takes place in a chemical vapor deposition(CVD) furnace chamber set to very high temperatures (~1000°C) and an inert gas such as argon (Ar) is passed through the chamber to remove the volatile by-products which may have been formed. This 2006 report of TCVD

synthesized graphene opened a new graphene processing route which had unresolved issues such as minimizing the folds and controlling the number of layers^[96].

Deposition of graphene on Ni wafer was attributed to the good solubility of carbon in Ni and on carbon segregation kinetics. Cooling rates are also of vital importance, that is, at slow cooling rates carbon does not segregate on the metal surface: moderate cooling rates allow carbon segregation, and at high cooling rates carbon segregates out of Ni and forms less crystalline and defective graphite structures^[97].

Wang *et.al*^[98] grew graphene on a ceramic boat using an MgO supported Co catalyst and CH₄ hydrocarbon gas. The MgO and Co were washed off with concentrated hydrochloric acid (HCl) and distilled water. The resulting graphene structure was confirmed by high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), and Raman spectroscopic analysis. The graphene produced this way is substrate free.

Other attempts at growing substrate free graphene have been carried out. They include evaporating Ni on a SiO₂/Si substrate, annealing it to produce Ni grains, and finally growing graphene on these grains. This graphene could be transferred to any other substrate without changing or damaging any of its properties (e.g. electrical and optical properties). This enables it to be used in electronic applications^[99].

2.6.2.1.2. Thermal Decomposition of Silicon Carbide (SiC)

This method employs silicon carbide (SiC), whose carbon is reduced to graphene by simply exposing the wafer to high temperatures (1250-1450 °C) for short periods of time (1-20 minutes). Three-layer graphene sheets were produced in this process. This is a temperature dependent technique, as one atom thick graphene films are produced at low temperatures^[100].

Thermal decomposition of SiC led to thermal decomposition of organics on other substrates such as transition metals. This is an advantage when coming to applications such as manufacturing of sensors and electronics^[101].

2.6.2.1.3. Plasma Enhanced Chemical Vapour Deposition (PECVD)

Plasma enhanced chemical vapour deposition is another technique which could be used to synthesize graphene at lower temperatures ($<1000\text{ }^{\circ}\text{C}$) in a very short amount of time (<5 minutes) as compared to the TCVD^[102,103]. The first PECVD synthesis of graphene which had single- to few- layers involved radiofrequency systems to synthesize graphene on different substrates such as silicon (Si), tungsten (W), molybdenum (Mo), zirconium (Zr), titanium (Ti), hafnium (Hf), niobium (Nb), tantalum (Ta), chromium (Cr), silicon dioxide (SiO_2), aluminium oxide (Al_2O_3), and 304 stainless steel with no prior treatments of the substrate surfaces. A gas mixture of 5-100% methane and hydrogen gases at total pressure of 12Pa, at 90W, and substrate temperature of 680°C produced a subnanometer thick graphene. The ease of this method attracted the attention of the scientific community. The PECVD do not limit the field applications of graphene because they allow its deposition on a wide range of substrates^[104-107].

2.6.2.1.4. Unzipping The Carbon Nanotubes (CNTs)

Carbon nanotubes are graphene in its one dimensional form (the rolled form). These rolls can be opened-up to form two dimensional carbon plane graphene, thus there have been many studies of CNTs openings lately^[97,108], (figure 2.9). The very first method of unzipping CNTs involved the longitudinal multiwall nanotubes (MWNTs) opening by using intercalation of lithium (Li) and ammonia (NH_3), followed by acid exfoliation and thermal treatments. The resulting product consisted of nanoribbons, partially opened MWNTs, and graphene flakes, (figure 2.9a)^[109].

The other approach of producing graphene nanoribbons (GNRs) by unzipping the CNTs involves oxidation and longitudinal unzipping of MWCNTs in a mixture of concentrated sulphuric acid, potassium permanganate, and hydrogen peroxide. This process produced GNRs which are highly oxygenated and therefore a hydrazine monohydrate and ammonium hydroxide solution was used to reduce the oxygenated GNRs, thus restoring their good electrical conductivity, (figure 2.9b)^[110]. Shimizu's group^[111] used the above procedure to oxidize and exfoliate the MWCNTs and used a three step annealing treatment at 800°C ; 750°C , and $300\text{ }^{\circ}\text{C}$ to remove the

oxygen moieties. The HRTEM studies indicated incomplete removal of oxygen functional groups and thus the more structural defects associated with oxygenation.

Graphene layers were also synthesized via catalytic unzipping of CNTs. In this method, metal nanoparticles (Co or Ni) are deposited on the surface of CNTs. The metal coated CNTs are then placed on Si wafers and heated at 850°C under an H₂- Ar atmosphere (figure2.9c)^[112-114]. In this technique the nanostructured metal dissociates the C-C bonds and the carbon atoms ultimately react with the H₂ and form methane (CH₄)^[115].

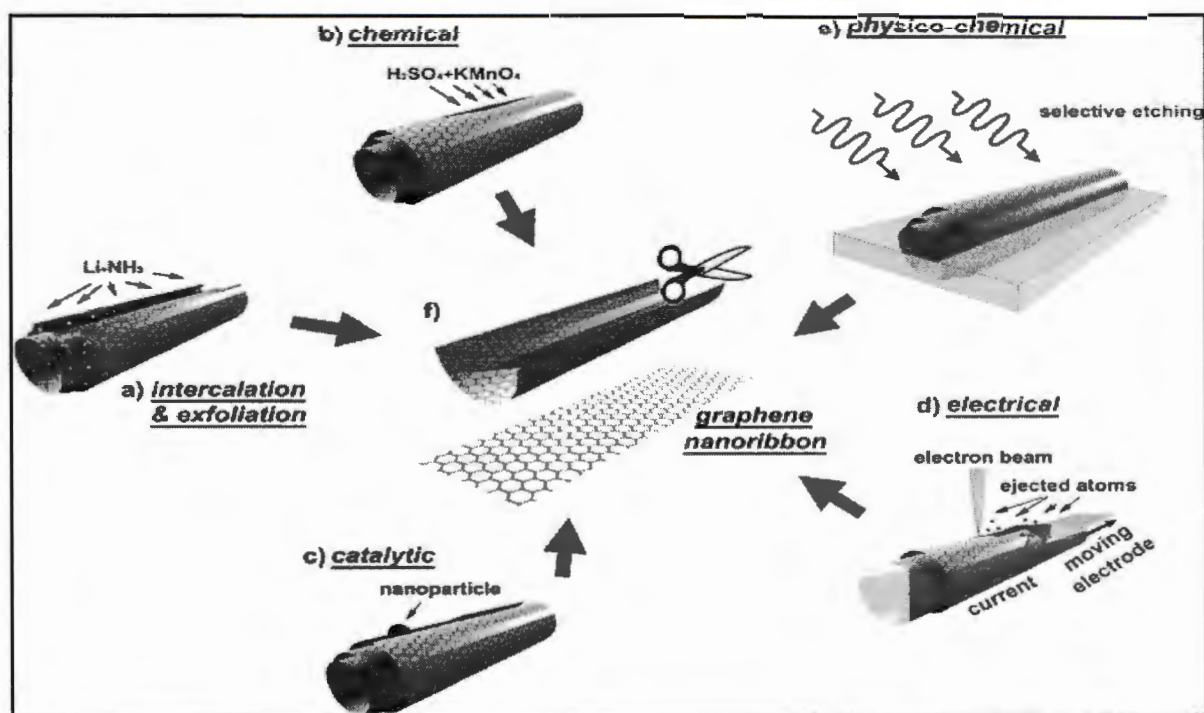


Figure2.9: Schematic representation of the method used for unzipping carbon nanotubes to form graphene^[108]

Alternatively, an electrical current could be used to unwrap the CNTs to form GNRs (figure2.9d). This method offers a cleaner way of inducing CNTs because it does not involve chemicals. Kim *et al*^[116] produced GNRs by using in situ method meaning that there is CNTs unzipping and characterization at the same time. They introduced the MWCNTs into the TEM and used 100KeV to open the tubes. During this process only the outer wall is being ruptured and as this happens, the inner core slides out. GNRs produced this way have high current carrying capacity.

Jiao *et al* ^[117] developed a method of producing GNRs through controlled unzipping of CNTs using an argon plasma etching method (figure 2.9e). They simply embedded the MWCNTs in an etch mask (polymethacrylate (PMMA) on a silicon substrate, followed by baking. Then potassium hydroxide (KOH) solution was used to peel off the PMMA-MWCNT film, leaving the narrow strip of MWCNT sidewall exposed to a low Ar plasma treatment. This method could produce the GNRs and GNRs with inner CNT cores which are mono-, bi-, and multi-layered, depending on the number of layers of the starting MWCNT and etching time. The PMMA was removed by acetone vapour followed by calcinations at 300°C to produce GNRs on the Si substrate. Atomic force microscopy (AFM) images showed that these GNRs have smooth edges and uniform width of 10-20 nm.

2.6.2.2. TOP-DOWN GRAPHENE

This involves breaking down bulk materials to form nanostructures. Traditional ways of producing materials could be modified to produce the end-product in nanoscale dimensions. This method produces nanoparticles in large amounts and is therefore suitable for making polymer nanohybrids. Top-down processes are more economically advantageous because of the availability of graphite or its derivatives. Generally, graphene or chemically modified graphene are produced by separation or exfoliation of graphite and its derivatives (graphite fluoride), that is, fabricating colloidal suspensions and microexfoliation of graphite are used to synthesize graphene^[95].

2.6.2.2.1. Exfoliation and Cleavage

Graphite is a three dimensional (3D) stacked layer of graphene sheets. These layers are bound together by weak Van der Waals forces or interactions, which could easily be broken to produce individual graphene sheets. Exfoliation and cleavage employ either chemical or mechanical energy to break-up these interactions^[97]. A problem is encountered, however, in achieving homogeneous, individual graphene sheet dispersions in different solvents. This is because graphene sheets tend to restack into graphite or form irreversible agglomerates through Van der

Waals forces^[15]. So there is a need to prevent agglomeration and restack because the properties of graphene are dependent on each individual sheets.

Mechanical exfoliation also known as micromechanical exfoliation is a process in which scotch tape is used to repeatedly split graphitic crystals into thinner pieces (figure 2.10). Typically, the commercially available highly oriented pyrolytic graphite (HOPG) is subjected to dry etching in oxygen plasma to make many five micrometer deep mesas which are then stuck on the photoresist and layers are peeled off by Scotch tape. The tape attached optically transparent flakes are then released into acetone (propanone) and then sedimented on a Si wafer. This method produces high quality graphene which has near ideal crystal structure, but is labour intensive, and is not suitable for industrial production^[17].

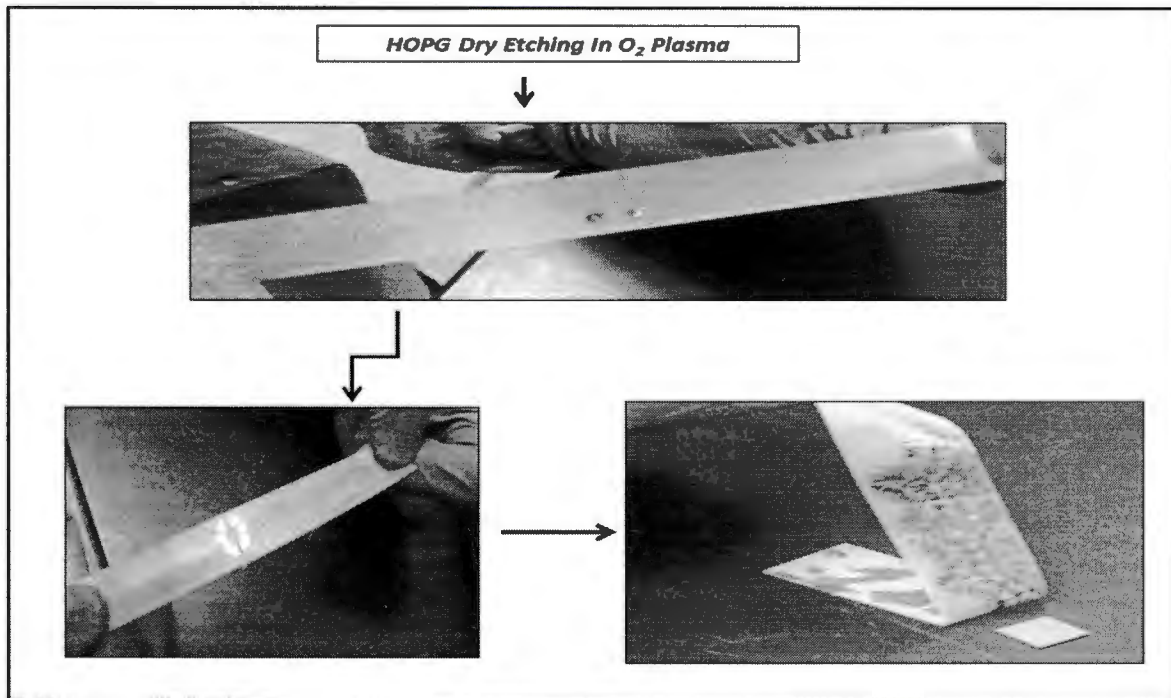


Figure 2.10: Micromechanical exfoliation of graphite.

Another method uses liquid phase exfoliation. Stankovich *et al*^[118,119] utilized the hydrophobicity of graphite and exfoliated graphite oxide (GO) nanosheets in an attempt to reduce them with hydrazine hydrate. The final product was not fully reduced meaning that it had structural defects which disrupt the electrical conductivity and carrier mobility of graphene. Therefore, liquid phase exfoliation of graphite and its derivative could be used to maintain the graphene

structure^[118-120]. This method is only viable if the right solvent or solvent mixture is able to form graphene-solvent interactions which can overcome the Van der Waals interactions in between the graphene sheets^[121]. Thus dispersion and exfoliation of graphite in organic solvents such as N-methylpyrrolidone (NMP), was invented to produce fully reduced single- to few- layered graphene sheets. Such techniques utilize solvent-graphene interaction; the graphene and solvent must have similar surface energy^[122,123]. This approach has the promise of large scale graphene production but has the disadvantages of high cost of the solvent and difficulty of graphene deposition due to the solvent's high boiling point^[97].



Interaction of small molecules by mechanical exfoliation is used to prevent agglomeration of graphite layers by simply inserting small molecules or non-covalently attaching polymers in between the graphite, thus generating graphite intercalated compounds (GIC). Covalent attachments are not used because they disrupt the sp^2 conjugation system of graphite and hence decrease its electrical conductivity.

Li *et al*^[124] produced a highly conductive graphene by using a graphite exfoliation-reintercalated-expansion method. Because it is easier for oxidants or molecules to be incorporated between the expanded (thermally expanded) graphite (EG) interlayers than unexpanded ones, Li *et al* subjected commercial expandable graphite to sixty seconds heating at one thousand degrees Celsius in fuming gas. The EG was grounded with sodium chloride and reintercalated with oleum, followed by dispersion in N,N-dimethylformamide (DMF) and tetrabutylammonium (TBA) treatment. TBA facilitates the separation of graphene sheets in surfactant solution by being inserted into and hence increasing the distance between adjacent graphite layers.

2.6.2.2.2. Chemical Methods of Synthesizing Graphene

The chemical methods produce large quantity graphene. This production method is based on the exfoliation and reduction of graphene oxide. The Brodie, Staudenmaier and Hummers methods are used to oxidize graphite using strong oxidants and acids^[77-80]. The produced graphene oxide could then be reduced using either chemical, thermal or electrochemical methods^[118,125-127]. The first chemically produced graphene was reported by Horiuchi *et al*^[128] who produced carbon nanofilms (CNF) from natural graphite by a series of oxidation and purification processes,

followed by dilution steps which lead to extraction of the thinnest sheets from the dispersion. The CNF's thickness was found to be directly related to the dilution factor and the product consisted of one-to-six layers.

2.6.2.2.3. Synthesis of graphite oxide

Graphite is a three-dimensional carbon allotrope which occurs naturally as either crystalline flake, meta-anthracite (amorphous), or lump (vein). For chemical reaction purposes graphite is purified in order to remove heteroatomic contaminations^[129-130]. As highlighted above graphite oxide has been synthesized as far back as 1859 when Brodie was studying graphite structure by investigating the graphite flake's reactivity. His technique of synthesizing graphite oxide involved adding graphite into a mixture of concentrated nitric acid (HNO₃) and potassium chlorate (KClO₃). He found that the material produced consisted of carbon, hydrogen, and oxygen which increased the overall mass of graphite, and that this material is dispersible in water but not in acidic medium and then decided to refer to it as "graphic acid". After heating the material which was found to be C_{2.19}H_{0.080}O_{1.00} at high temperatures of 220°C its composition changed to C_{5.51}H_{0.048}O_{1.00} and declared "this form of carbon should be characterized by a name marking it as a distinct element, I propose to term it "Graphon"^[77].

Thirty nine years later Staudenmaier modified Brodie's graphite oxidation method by adding multiple aliquots of chlorates accompanied by increasing the acidity of the reaction mixture by additions of concentrated sulphuric acid, which resulted in an overall extent of oxidation similar to that of Brodie's multiple oxidation approach^[78]. Sixty years after Staudenmaier, Hummers *et al.*^[79] used a mixture of sodium nitrate (NaNO₃), potassium permanganate (KMnO₄), and sulphuric acid (H₂SO₄) to oxidize graphite, and they achieved oxidation levels similar to those of Brodie and Staudenmaier^[79]. Other scientists developed graphite oxidizing methods which are based on the above mentioned methods.

2.6.2.2.4. Reduction of graphite oxide

Graphene oxide is heavily oxygenated with hydroxyl and epoxy groups which are located on the sp³ carbons on the basal plane and with the carboxyl and carbonyl groups which are located on

the sp^2 carbons. This together with the Zeta potentials (which are due to the ionization of carboxylic acid and hydroxyl groups) makes the graphite oxide to be hydrophilic and to be readily dispersed in water^[101,131]. Although graphite and graphene oxide have chemical properties which are similar (i.e. surface functional groups) their structures are different. That is, graphene oxide is a single to few layered material produced by exfoliation of graphite oxide^[132]. Graphite oxide can be exfoliated to graphene oxide using various thermal and mechanical routes but sonication and stirring GO in solvents such as water, NMP, DMF, and THF are most commonly used^[133].

The exfoliated monolayers of graphite oxide can be chemically reduced with various reducing agents such as hydrazine^[118,120,134] and sodium borohydrate^[135]. Hydrazine has been found to be the best reductant of graphene oxide because it doesn't have any reactivity with water^[102]. During the reduction process, graphite oxide monolayers become black and then start to agglomerate and precipitate^[118,134]. The process of precipitation is attributed to the fact that the reduction process diminishes the hydrophilic character or depletes the oxygen atoms that give the graphene oxide its hydrophilic characteristic. Stankovich proposed a graphene oxide reduction by hydrazine pathway (figure 2.11)^[118].

This pathway suggests that the mechanism of reduction of GO using hydrazine is similar to the selective elimination reactions of ketones to form aminoaziridine, and forms hydrazine alcohol, which will undergo further reactions of ketones. What actually happens is that the hydrazine hydrate opens the epoxides and forms hydrazine alcohol, which undergoes further reactions and form an aminoaziridine. The diimide in the aminoaziridine will then be eliminated in a process of thermal diimide elimination and as this happens, the C=C bond is formed^[136-138].

Hydrazine does not completely reduce all the oxygen moieties found in the graphene oxide, that is, it removes all the epoxy and hydroxyl groups but leaves the carboxyl and carbonyl groups at the edges^[139-141]. Few methods of removing the remaining oxygen moieties are available. Gao *et al*^[139] exposed the hydrazine reduced graphene oxide to concentrated sulphuric acid to remove the edge oxygen moieties.

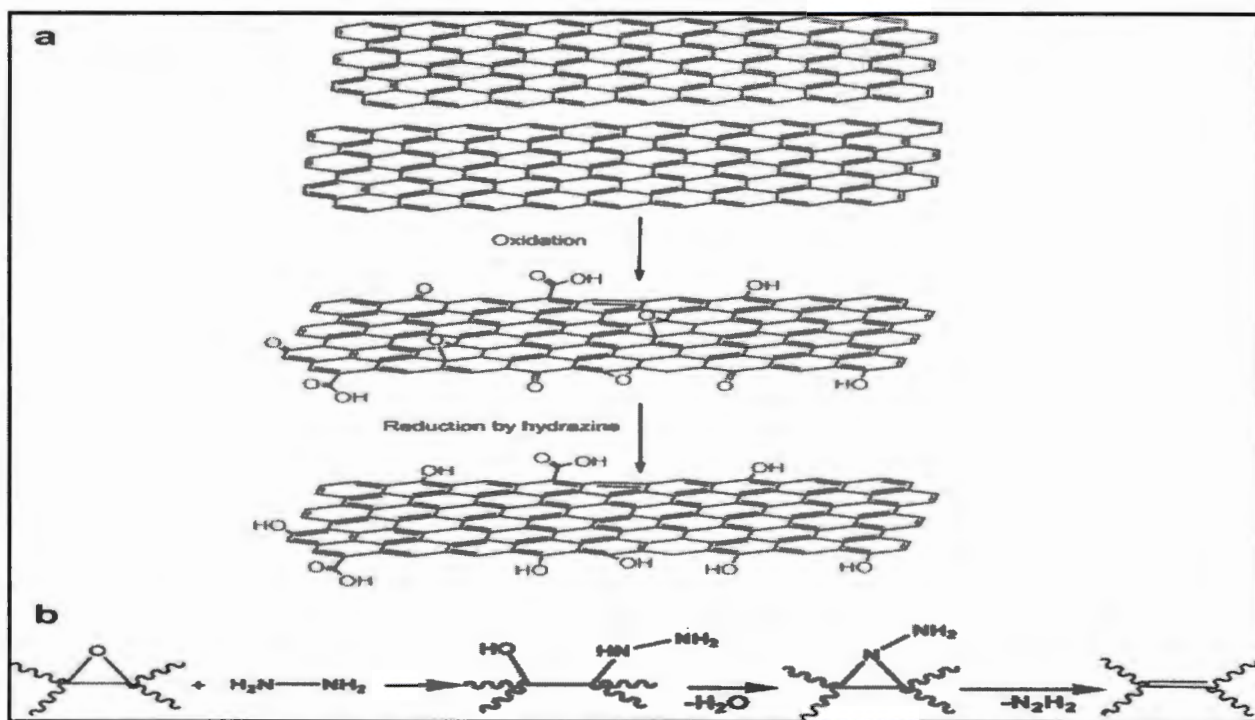


Figure 2.11: Oxidation of graphite to graphene oxide and reduction to reduced graphene oxide. (b) A proposed reaction pathway for epoxy reduction by hydrazine^[118].

Li *et al*^[131] considered that electrostatically stabilized dispersions of colloids are dependent on parameters such as the content of dispersed particles, pH, and electrolyte concentration. They therefore decided to control the parameters in order to synthesize a stable colloid of graphene. They adjusted the pH of the water, hydrazine, and graphene oxide mixture to around ten with ammonia solution which aided in the deprotonation of carboxylic acid groups, thus the (Zeta potential) electrostatic repulsion among the charged groups on reduced graphene oxide enabled the formation of colloid graphene sheets in water.

Though sodium borohydride hydrolyzes in water, it is a better reductant than hydrazine because it removes all the oxygen functional groups found on the graphene oxide surface. When sodium borohydride is used as a reductant, the reduced graphene oxide could have a low resistance of 59 $\text{k}\Omega/\text{sq}$ as compared to the one in which hydrazine was used ($\sim 780 \text{ k}\Omega/\text{sq}$), and the carbon to oxygen ratio of 13.4:1 as compared to 6.2:1 for hydrazine^[135,142].

Thermal reduction is another method of reducing GO; it simply employs exposing the GO to high temperatures. When GO is heated at high temperatures ($\sim 1050^\circ\text{C}$) exfoliation occurs when

the pressure of the CO₂ evolved exceeds the Van der Waals forces. The Hamaker constant was used to numerically predict that a pressure of 2.5 MPa is required to separate the stacked graphite oxide sheets. AFM studies revealed that the 30% mass loss leaves behind the vacancies and the topological damages or defects, which may affect the mechanical and electrical properties of the reduced graphene oxide^[125,143]. Nevertheless, the conductivities of the reduced GO were measured to be 1000-2300 Sm⁻¹, suggesting effective overall GO reduction and restoration of the plane's electronic structure from GO^[125].

Electrochemical reduction is a new method which is used to remove the oxygen moieties on the graphene oxide via an electrochemical route. This method is advantageous because it doesn't use environmentally hazardous reductants and there are no by-product disposals. Generally, graphene oxide is deposited on a substrate, followed by placing electrodes at opposite ends of the graphene oxide mounted substrate, and running linear sweep voltammetry in a sodium phosphate buffer solution between -0.60 to -0.87 V. Rapid reduction was observed during the first five minutes (300 seconds) after which slower reduction followed. Carbon elemental analysis revealed that the product had a C: O ratio of 23.9:1, with a conductivity of ~8 500 Sm⁻¹^[127].

2.6.3. SURFACE MODIFICATION OF GRAPHENE

Graphene has the tendency to restack or to agglomerate which makes it unsuitable for intercalation by large molecules^[118,144]. Its chemical functionalization improves its processability, solubility, and interaction with polymer^[145,146], thus several graphene functionalization studies have been conducted. These studies include isocyanate modification^[118], amination esterification^[143,146], polymer wrapping^[119,147,148] and electrochemical modification using ionic liquids^[14].

2.6.3.1. CHEMICAL MODIFICATION

This employs chemical methods that are used to obtain soluble graphene after oxidizing graphite. These methods are reduction of graphite in a stabilization medium, covalent modification, non-covalent functionalization of reduced GO, nucleophile substitution, and diazonium salt coupling.

The non-covalent functionalization exhibited by graphene oxide (GO) comes from the weak interactions which are due to π - π stacking, Van der Waals interactions, and electrostatic/cation- π interactions between itself and the target molecules. These interactions are located on the sp^2 networks that are not oxidized or engaged in hydrogen bonding. During the chemical reduction of GO, there is an irreversible agglomeration of particles which could even after long sonication or stirring not be re-dispersed, but this problem could be ameliorated by reduction of GO in the presence of non-covalent functionalizing molecules^[119]. This will at last produce functional composite materials. The π - π stacking between the GO and the conjugated polymers (such as sulfonated PANI^[147] and poly(3-hexylthiophene) (P3HT)^[149]) or aromatic compounds (such as 7,7,8,8-tetracyanoquinodimethane (TCNQ) anion^[150] and tetrasulfonate salt of copper phthalocyanine (TSCuPc)^[151]) can stabilize the chemically reduced GO (RGO). These interactions between the RGO and the target molecules (aromatic compounds and conjugated polymers) do not disturb the electronic properties of the RGO. For example, layers of RGO were stabilized by incorporating TSCuPc-grafted RGO in between them, hence making them to be water dispersible. AFM images of the TSCuPc-grafted RGO indicated that it has a thickness of ~ 1.9 nm, whereas the RGO has a thickness of ~ 1 nm and AFM height analysis confirmed the non-covalent attachment of TSCuPc on the RGO basal plane/ sp^2 network via π - π stacking^[151-152].

In nucleophilic substitution, the epoxy/ epoxide functional groups are the site on the GO where nucleophilic substitution occurs. During the preparation of the aliphatic amine modified GO, the grafting of small chain primary amine ($C_nH_{2n+1}NH_2$ (where $n=2, 4, 8, 12$)) could be completed at room temperature while that of long aliphatic amines are completed under reflux for 24 hrs (completed at elevated temperatures)^[153]. The short chain primary amine grafted GO is dispersed more easily than the ones with long aliphatic amines, in organic solvents. The interlayer distance of amine chain grafted GO is dependent on the length of the amine chain as well as on their orientation relative to the layers, thus tilted orientations are due to hydrophilic characteristic of the GO layers^[142].

Some of the methods used for covalent functionalization of graphene oxide have been adapted from those which are used for carbon nanotubes. These methods include esterification or amidation. The surface of GO could be modified by treatment with organic amines^[145], isocyanates^[153], alkyl lithium reagents^[146], diisocyanate compounds^[154], etc. These agents tend to

make GO less hydrophilic by forming carbamate ester and amide bonds with carboxyl and hydroxyl groups respectively (figure2.12). The modified GO forms stable dispersions in polar aprotic solvents, and this is advantageous because graphene monolayers and intimate GR/polymer nanocomposites could be produced from these dispersions^[153].

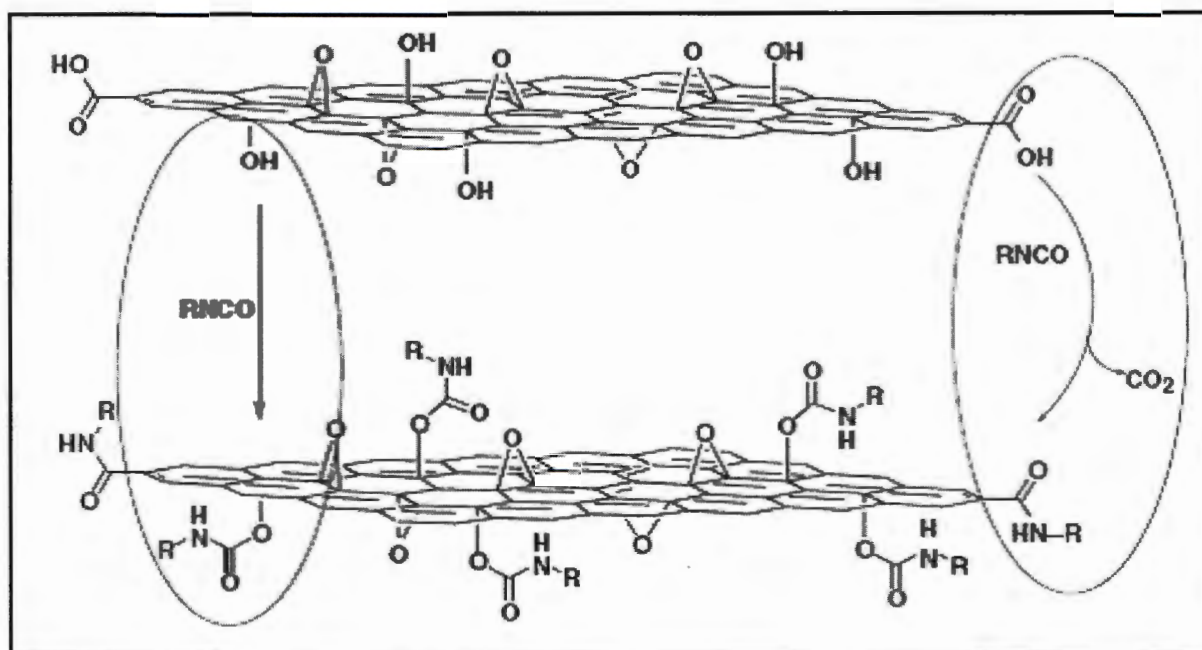


Figure2.12: The isocyanate treatment of GO where organic isocyanate reacts with the hydroxyl groups of the graphene oxide^[153].

The carboxyl groups on the GO surface have been utilized to anchor GO to other molecules by simply activating them using agents such as 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC)^[155], 2-(7-aza-1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HATU)^[154], thionyl chloride (SOCl₂)^[145,156], or N,N-dicyclohexylcarbodiimide (DCC)^[157]. The subsequent addition of species which are nucleophilic (e.g. amines or hydroxyls/alcohols) produced covalently attached functional groups on the GO via amide or ester formation. Amine functionalized GO has been used in different applications such as in drug delivery vehicles, polymer composites^[155], optoelectronics^[156] and biodevices^[158].

The attachment of long, hydrophilic, and aliphatic amine groups on the GO enhanced the dispersibility of the chemically modified GO in organic solvents^[146], whereas the addition of

porphyrin-functionalized primary amines and fullerene-functionalized secondary amines introduces amazing non-linear optical performance^[159].

The reduction of graphite oxide in a stabilization medium enables the synthesis of stable graphene dispersions without the need for polymers or surfactants as stabilizers. Park *et al*^[160] managed to produce graphene dispersions with good electrical conductivity by reducing graphene oxide which had been treated with an aqueous solution of potassium hydroxide (KOH). First they oxidized the graphite flakes (figure 2.13a) and then they treated the GO with KOH (figure 2.13b). Their argument was that KOH confers large negative charge through all oxygen containing groups found on the surface of graphene oxide sheets, and that the resulting GO sheets were coated with negative charges and potassium cations (K^+) which they called potassium hydroxide modified oxidized graphene (KMG).

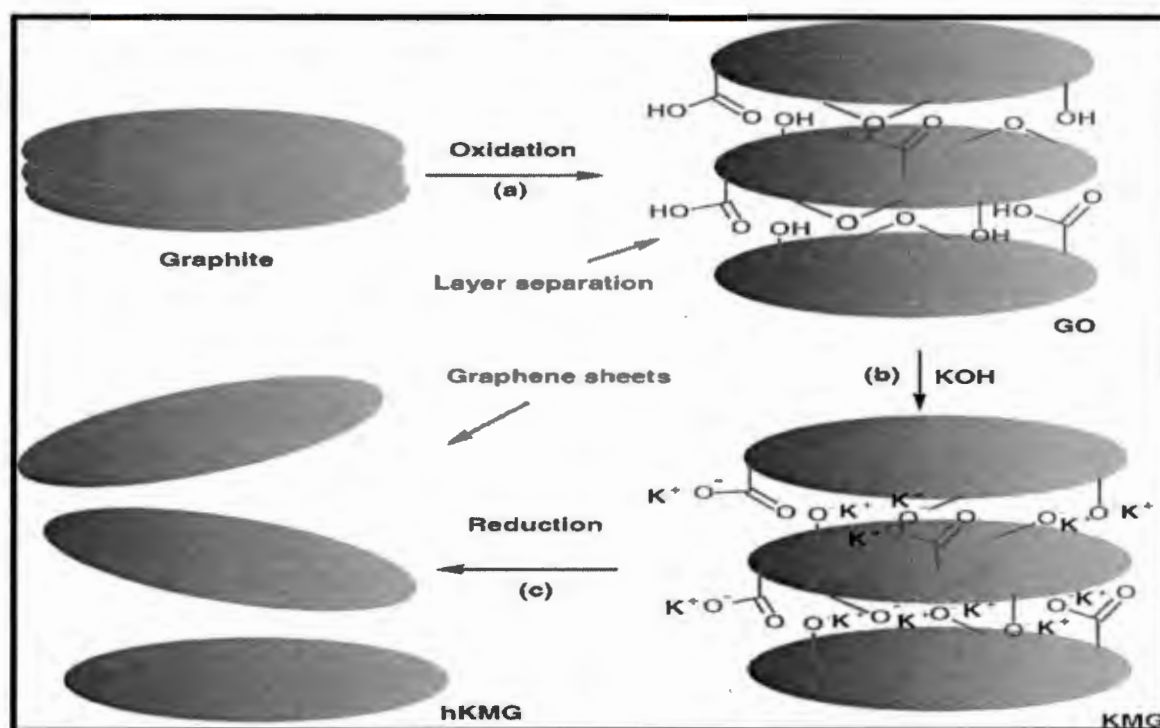


Figure 2.13: A simple route for the preparation of a homogeneous aqueous suspension of graphene sheets from graphite stack^[160].

After reduction by hydrazine monohydrate, they referred to the material as homogeneous hydrazine reduced KOH modified graphene (hKMG), (figure 2.13c). Li *et al*^[131] prepared stable

aqueous suspensions of GO sheets by adding ammonia solution to the graphene oxide dispersions during reduction by hydrazine.

2.6.3.2. ELECTROCHEMICAL MODIFICATION OF GRAPHENE

Colloidal suspensions of chemically modified graphene could be produced by treating graphite electrochemically (figure 2.14). A 10-20V potential is supplied to the electrodes which are immersed in a phase separated mixture of water and imidazolium based ionic liquids. Commercial graphite is used as a cathode electrode and after some time, ionic graphene functionalized sheets precipitate at the graphite anode. Then the precipitate is dried and

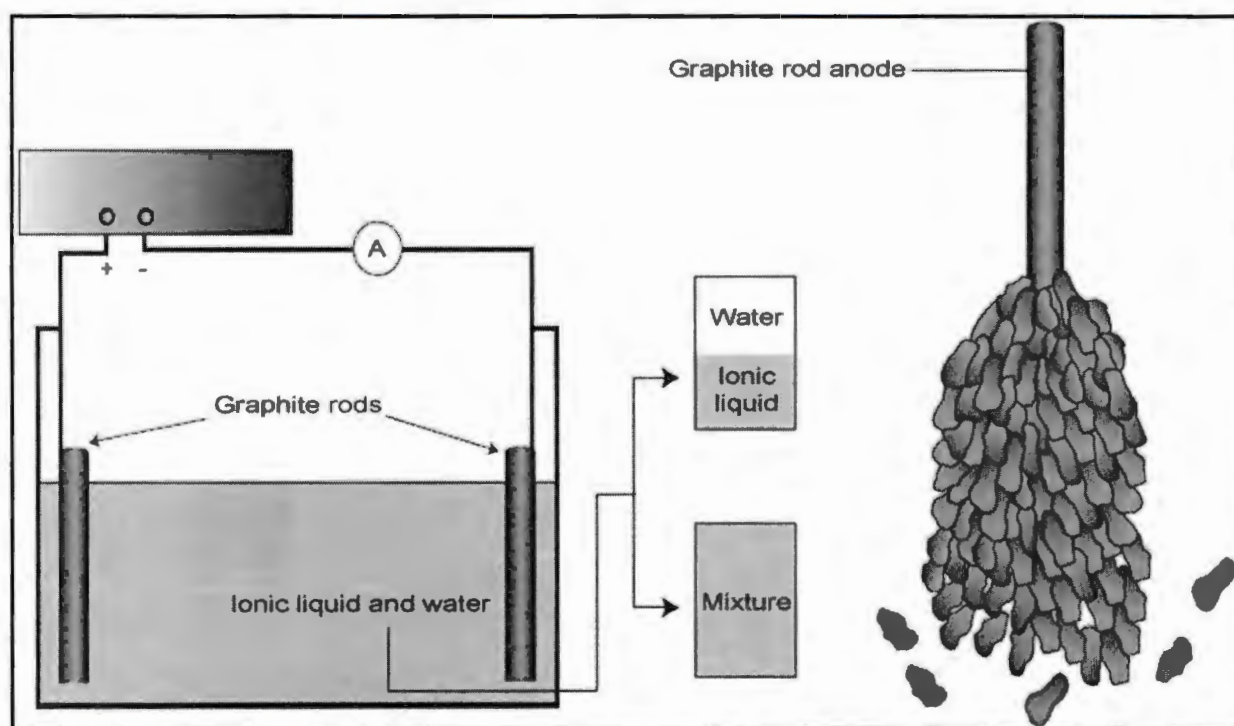


Figure 2.14: Experimental set-up (left) diagram for the electrochemical modification of graphene by ionic liquids and exfoliation of the graphite anode (right) to graphene^[14]

ultrasonicated in dimethylformamide (DMF) and the resulting compound is collected as a homogeneous graphene dispersion^[14].

2.6.3.3. π - π INTERACTION

This (π - π interaction) modification is based on the π - π interaction of pi-orbitals of graphene and the doping polymer. An aqueous solution of graphene is added to a solution of monomer and solvent and graphene is dispersed by sonicating the mixture in an ice water bath. The properties (mechanical, electrical, and thermal) of graphene make it a good nanofiller for making high performance nanocomposites^[161]. Thus polymer incorporation into the graphene structure is useful to go because it takes an advantage of the π - π interaction.

2.6.4. PROPERTIES OF GRAPHENE

Since its discovery, it has been known that graphene has desirable and unique electrical, optical, and mechanical properties. Some of these remarkable properties that have been reported include high values of its Young's modulus ~ 1.0 TPa, fracture strength of ~ 125 GPa, thermal conductivity ~ 5000 $\text{W m}^{-1}\text{K}^{-1}$, mobility of charge carriers $\sim 2000,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, quantum hall effect (transport phenomena), specific surface area ~ 2630 $\text{m}^2 \text{ g}^{-1}$ and a breaking strength of $\sim 40 \text{ Nm}^{-1}$. Measurements have shown that graphene is about 100-200 times stronger than steel although it is the thinnest material possible which makes it the strongest material ever tested^[18,162,163].

2.6.5. APPLICATIONS OF GRAPHENE

Graphene's extreme properties enable it to be used in a wide variety of applications such as in transmission microscopy (which requires thin, conductive, and strong materials to support delicate materials under study) and high frequency transistors (which need highly mobile charge carriers to operate). It could also be used in manufacturing single molecule gas detectors (due to its 2D structure), nanoribbons (due to its 2D structure, high electrical and thermal conductivity, and low noise), transparent conducting electrodes (due to high optical transparency and high electrical conductivity), ultracapacitors (due to high surface area to mass ratio), and chemical and biosensors (due to large surface area, atomic thickness, molecularly-gatable structure and its modifiable chemistry)^[97,163].

2.7. GRAPHENE BASED NANOCOMPOSITES

Composites are materials which are engineered or naturally occurring materials made from two or more constituents with significantly different physical or chemical properties which remain separate and distinct at macroscopic and microscopic scale within their finished structure. These materials are able to perform tasks that the individual materials cannot perform by themselves. Thus, several successful attempts to hybridize graphene with other materials such as polymer and nanoparticles of metals, metal oxides and semiconductors have been carried out. These nanocomposites have shown many applications in a broad spectrum, such as in fuel cells, supercapacitors, batteries, and photovoltaic devices^[163].

2.7.1. SYNTHESIS OF GRAPHENE NANOCOMPOSITES

Both the graphene and carbon nanotube polymer composites have been proved to have similar mechanical properties but the graphene/polymer composites have highly enhanced thermal and electrical conductivities and larger surface areas^[164]. The enhanced properties found in the graphene/polymer hybrids arise from the high reinforcement of graphene nanofillers^[165]. Because the nanostructured polymers have improved properties and performance, the graphene/nanopolymer composites show better properties than polymers that have been synthesized using traditional oxidative methods^[166].

The interaction in graphene/polymer composites depends upon the molecular weight, hydrophobicity, polarity and reactive groups present in the polymer and graphene as well as in the solvent^[118]. There are three methods of synthesizing graphene/polymer nanocomposites and they are: in situ intercalative polymerization, solution and melt intercalation methods.

In in situ intercalative polymerization methods graphene or modified graphene is dispersed in a liquid monomer in order to get it swollen. This dispersion and swelling are then followed by the addition of an initiator/oxidant into the graphene-monomer mixture. Heat or radiation is used to initiate the polymerization process^[167].

Solution intercalation is based on a solvent in which the polymer is solubilized. Graphene layers are allowed to swell in the polymer/solvent solutions, and then the solvent is removed^[168]. High power ultrasonication could be employed to form individually dispersed graphene sheets but long time exposure reduces the properties of the composites by inducing defects in the graphene sheets. Due to weak Van der Waals forces that stack graphene layers together it is possible to disperse graphene in common solvents such as tetrahydrofuran (THF), dimethyl formamide (DMF), chloroform, water, toluene, or acetone. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated, the sheets reassemble, sandwiching the polymer to form nanocomposites^[169]. Slow solvent evaporation causes graphene to agglomerate, resulting in the formation of inhomogeneous distribution graphene sheets in polymer matrixes. Drop casting and spin coating are used to control the evaporation time and hence improve the distribution of graphene sheets in the polymer matrix^[170].

The entropy gained by desorption of solvent molecules serves as the driving force for polymer intercalation from the solution. This method allows the synthesis of intercalated composites based on polymers which have low or no polarity character^[171].

The Melt intercalation method involves no solvent. Graphene or graphite and polymer are mixed in the molten state. Extrusion and injection molding could be employed to mix thermoplastic polymers and graphene at high temperatures^[172]. Nanocomposites are then formed by intercalating or exfoliating the polymer chains. Melt intercalation is suitable for polymers which are unsuitable for adsorption (solution intercalation), or in-situ polymerization and is used mainly for thermoplastic polymer nanocomposite preparation^[172,173].

2.7.2. GRAPHENE/POLYANILINE NANOCOMPOSITES

Zhang *et al*^[167] prepared GR/PANI nanocomposites using the in situ intercalative method. In their study, they used different mass ratios of aniline: GO. After the polymerization of PANI in the presence of GO, the composites contained 10, 50, and 80% of GO and they were named PAGO 10, 50, and 80 respectfully. After the reduction of GO within the composites by hydrazine the composites were then stirred in the APS and 1M HCl solution to recover PANI (by reoxidation and reprotonation processes) and the final products were named PAG 10, 50, and 80

respectively. The analytical characterization of these composites by SEM and TEM showed that in PAGO/PAG 10 and 50, PANI was either homogeneously surrounding or distributed on the surface or between the GO/GR sheets. The PANI in PAGO/PAG80 was less and was either adsorbed on the surface or intercalated between the GO/GR sheets. The selected area electron diffraction (SAED) patterns revealed that the crystallinity of composites increased with increasing GR ratios. The FTIR spectra showed that the PAGO composites had the 1700 cm^{-1} peak which is due to the C=O group of GO, 1577 and 1135 cm^{-1} peaks which are due to quinoidal rings (C=N and -NH^+ respectively), and a 1476 cm^{-1} peak which is due to the benzoid ring. After reduction of PAGOs, the 1700 cm^{-1} peak disappeared and that indicated the reduction of GO within the composites thus, the PAG composites exhibited the 1591 and 1161 cm^{-1} peaks which depict quinoidal rings and the 1497 cm^{-1} peak due to the benzoid ring. Thermogravimetric analysis (TGA) studies showed that the PAGO composites lost 30% mass at temperatures between $100\text{-}300\text{ }^{\circ}\text{C}$ which is due to the decomposition of oxygen moieties, whereas the PAGs lost 25% mass at temperatures between $100\text{-}600\text{ }^{\circ}\text{C}$ and most of this mass is due to decomposition of PANI above 300°C . The electrical conductivity of the pelleted composites was measured by a four-probe resistivity measurement system. In the PAGOs, there was a decrease in conductivity as GO ratios increased (i.e. PAG 10, 50, and 80 had conductivities of 231.2 , 17.5 , and 0.45 Sm^{-1} respectively). In PAGO10 this is attributed to high doping levels of PANI and to GO/PANI π - π stacking, while the decrease in conductivity of PAGO50 and 80 is caused by the insulating effect of GO. In the case of the PAGs the high conductivity of PAG10 (168.7 Sm^{-1}) is due to GR/PANI π - π stacking and is lower than that of PAGO10 because of the low doping degree of PANI after the reduction, reoxidation, and reprotonation processes. The conductivities of PAG 50 and 80 (22.8 and 143.0 Sm^{-1}) are higher than that of their unreduced counterparts because of the recovery of graphene which has a high conductivity of 277.2 Sm^{-1} .

Wu *et al*^[174] prepared GR/PANI composite films using the solution intercalation method. PANI nanofibres were prepared by the interfacial polymerization method whereas GR was recovered from GO which was prepared by Hummer's method by chemical reduction using hydrazine hydrate. The composite films were prepared by vacuum filtrating the mixed dispersions containing both PANI and GR. The composites contained the weight ratios (rG) of 20, 30, and 40 the GR/PANI₂₀ was fragile and the GR/PANI₄₀ shrunk dramatically after drying, whereas the

GR/PANI₃₀ was flexible, and it was therefore used for analysis. The SEM of the GR/PANI₃₀ showed that the PANI fibres were sandwiched between the GR sheets. This composite film had a conductivity of $5.5 \times 10^2 \text{ Sm}^{-1}$. Its cyclic voltammetry (CV) showed two pairs of redox waves which are attributed to the redox chemistry of PANI. The rectangular areas of the CV indicate that the composite has large double-layer capacitance.

2.8. IONIC LIQUIDS



As highlighted in chapter one, our lives are dependent on materials and technology, which unfortunately comes with a tremendously huge luggage of “dirt”. Its production involves the usage of chemicals such as volatile organic solvents which could be hazardous towards human beings and the environment^[175]. A memorandum of understanding was in 1992 signed by the United States to address the issue of hazards they are faced with, and this gave birth to what is known as “Green Chemistry”. This green chemistry has been addressed through outreach initiatives, research, implementation and education. In terms of research, Green Chemistry has been practiced in several industries such as in solvents, catalysis, polymers, renewables, analytical methods development, design of safer chemicals and the development of synthetic methods. To ensure a cleaner future, chemists had to re-evaluate chemical processes and devised several strategies for producing a “cleaner technology”. Regarding the solvent industry, the four main strategies are solvent free synthesis, use of water as a solvent, use of supercritical fluids, and most recently, the use of ionic liquids as solvents^[176].

Each of the first three strategies had some problems whereas the fourth one (which is the use of ionic liquids as solvent) is increasingly being applied in the chemical and synthetic industries. This is because ionic liquids are not only green but they also offer efficient product abstraction, have no or minimal waste, meaning that they have no or minimal disposal costs, and have remarkable properties^[176].

2.8.1. CHARACTERISTICS OF IONIC LIQUIDS

Ionic liquids are salts which are fluid over a varied temperature range, or liquid salts consisting of ion pairs ^[177-181]. These liquids are made-up of two ions in which one or both ions could be large. Normally, the cation is an organic ion which is bulky and asymmetric while the anions are either organic or inorganic ions. Thus the cations could, with different substitution, be based on phosphonium, pyrrolidinium, pyridinium, imidazolium, etc., while anions could be nitrate ($[\text{NO}_3]^-$), hexafluorophosphate ($[\text{PF}_6]^-$), $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$, alkyl sulphates, etc. ^[121,178,180]. Some common ionic liquid cations and anions are shown in figure 2.15. Ionic liquids can be simple, consisting of a single cation and anion (e.g. $[\text{EtNH}_3][\text{NO}_3]$), or binary, consisting of two salts at equilibrium (e.g. mixture of aluminium(III)chloride and 1,3dialkyl-imidazolium chloride salts) ^[178].

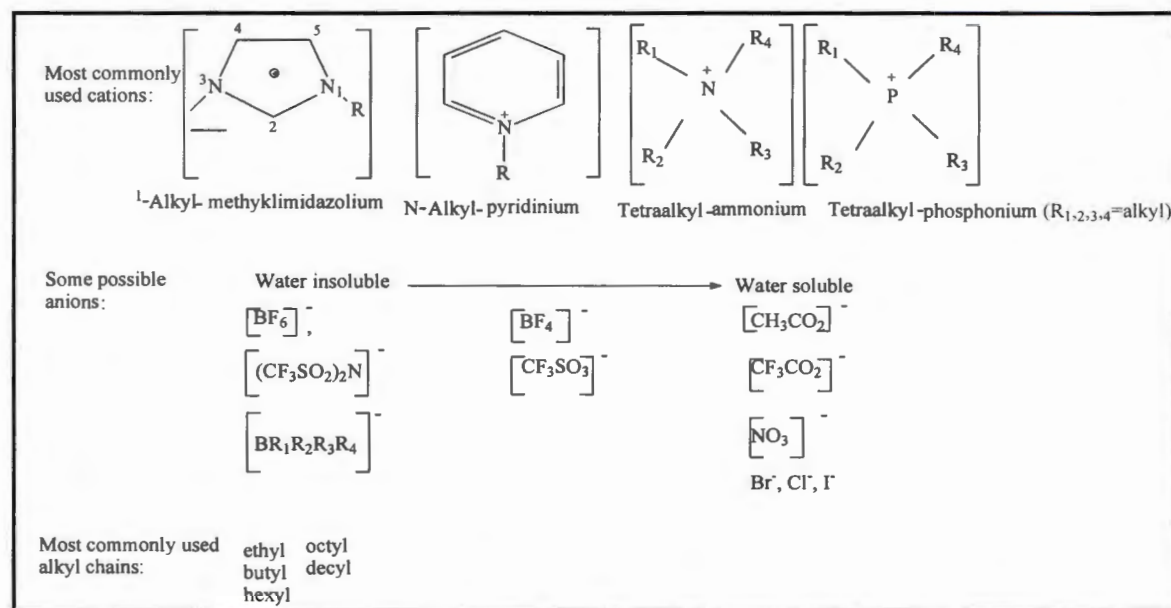


Figure 2.15: Some of the common ionic liquid cations and anions ^[178].

The exponential growth of interest in ionic liquids is due to their properties such as low/negligible vapour pressures, high viscosities; thermal stability and low melting points ^[177-181]. These properties enable them to be used as solvents for inorganic, organic and polymeric materials synthesis, electrochemical applications, liquid phase extraction and catalysis for clean technology ^[170].

Ionic liquids are sometimes termed “designer solvents”, because they can be designed to achieve certain specific properties. Their miscibility and thermal stability depends on the anion, while their viscosity and density depend on the side chain length in the cation. This means that depending on the choice of ions, it is possible to prepare ionic liquids at or below room temperature, for example ethylammonium nitrate $[\text{EtNH}_3][\text{NO}_3]$ has a melting point of 12 °C. The mutual electrostatic forces (of charged particles) in these liquids makes them miscible with polar solvents while their solubility in less polar solvents is determined by the alkyl chain in the cation, e.g. substituting PF_6^- with BF_4^- increases the solubility in water, and changing 1-alkyl chain from 1 to 10 on 1-alkyl-3-methylimidazolium hexafluorophosphate, $[\text{C}_n\text{MIm}][\text{PF}_6]$ makes it immiscible in water^[178,180].

Another most important thing about these liquids is that they are recyclable, so that minimal environmental contamination occurs during their production^[177,180].

2.8.2. PROPERTIES OF IONIC LIQUIDS

2.8.2.1. SOLVENT PROPERTIES

If ionic liquids are to be used as chemical reaction solvents, then their solvent properties should be studied. The most important property of a solvent is its polarity. A solvent is considered to be polar if it has the ability to solvate/dissolve and stabilize solutes. Their polarity could be measured by using solvatochromic probes which register solvent parameters such as hydrogen bond basicity (β), hydrogen acidity (α) and dipolarity/polarizability (π^*). The hydrogen bond basicity is determined by the anion present in a particular ionic liquid^[177,181].

2.8.2.2. PHYSICO-CHEMICAL PROPERTIES OF IONIC LIQUIDS

The structure and composition of ionic liquids is directly correlated to their melting points. Sizes of ions, cation symmetry, intermolecular interactions, and charge distribution determine their melting points. For example low symmetry cations are responsible for low melting point because they tend to minimize the lattice energy of the crystalline form of the salt. Excellent charge distribution and weak intermolecular interaction also decrease the melting point^[182].

The densities of ionic liquids are greater than that of water. The densities of ionic liquids are dependent on the ions used, thus the bulkier the cation, the smaller the density value^[183,184].

Most ionic liquids are said to be thermally stable at temperatures at or above 673K. This property is dependent on thermal decomposition of anions. Thermogravimetric analysis (TGA) scans are used to determine the thermal stability of ionic liquids under an inert environment^[185].

Ionic liquids could be used as solvents for both inorganic and organic reactions and in several applications such as electrochemical systems. Their viscosity is very important in this regard. It has been proven that high viscosity values are not good for chemical reactions because they tend to decrease the diffusion rates in oxidation-reduction reactions. Their viscosities could be decreased by adding low density solvents, e.g. Dichloromethane has been used to decrease the viscosity of [OMIM]^[177].

2.8.3. EFFECT OF IONIC LIQUIDS IN THE SYNTHESIS OF POLYANILINE AND GRAPHENE

Conventional appliances were proved to be not reproducible, thus several methods of manufacturing reproducible appliances, such as highly sensitive and selective sensors, have been invented. These new methods include utilization of nanoparticles which are believed to be hollow and have greater surface area and conductivity than previously employed bulky materials.

On the other hand, conventional solvents also needed to be changed. It was found that besides being hazardous to the environment, they can also cause some structural defects on the understudy material and these defects limit the material's applications. In order to minimize or completely cancel out these defects ionic liquids (ILs) were used, because of their wide electrochemical window, high ionic conductivity, thermal stability and low vapor pressure^[186].

2.8.3.1. IONIC LIQUIDS IN THE SYNTHESIS OF POLYANILINE

Shi *et al*^[187] used an electrochemical polymerization method to polymerize aniline in 1-ethyl-3-methylimidazolium ethyl sulphate [EMIES]. The cell was made-up of two platinum electrodes (of which one was the counter and the other one the working electrode), and the saturated

calomel electrode served as a reference electrode. A 1.2 V potential was applied to the electrodes and as time passed PANI started to be deposited on the surface of the working electrode. The FTIR spectra had the following peaks; 1580, 1490, 1295, 1140, and 800 cm^{-1} which are assigned to the stretching vibrations of quinine ring, benzene ring, C-N stretch in the secondary aromatic amine, aromatic C-H in-plane bending modes, and the C-H out-of plane deformation in the 1,4-disubstituted benzene ring, respectively. The UV-Vis and FTIR spectra of EMIES-PANI showed a similar frame-work to the HCl-PANI. The cyclic-voltammetry of EMIES-PANI has good electrochemical activity in a wide pH range.

Gao *et al*^[188] reported the synthesis of PANI nanostructures at the interface of 1-butyl-3-imidazolium hexafluorophosphate ([BMIM][PF₆] or [C4MIM]PF₆), which served as the organic phase, and hydrochloric acid (aqueous phase). They made a solution of aniline monomer by dissolving it in [BMIM][PF₆] and that of potassium peroxy sulfate in 1M HCl. The two solutions were mixed together in a beaker. After five minutes the emeraldine salt started to form at the interface of the two solutions, and then migrated into the aqueous phase because of its hydrophilic character. The polymer was collected by filtration, washed with ethanol and water, and then dried in a vacuum oven for one day. The TEM images showed that the nanoparticle had diameters of 30-80 nm. These PANI nanostructures had FTIR adsorption peaks at 1556.2 and 1489.7 cm^{-1} which are assigned to the stretching deformations of quinine and benzene ring respectively, while the 1293.3, 1142.1, and 821.1 cm^{-1} peaks are due to C-N stretch in the secondary aromatic amine, aromatic C-H in-plane bending modes, and the C-H out-plane deformations in the 1,4-disubstituted benzene ring respectively. This PANI has the electrical conductivity of 6.8×10^{-2} S/cm.

2.8.3.2. GRAPHENE IN IONIC LIQUIDS

Ionic liquids increase the applicability of materials by improving their performance and they have been used as electrode modifiers and as IL-carbon composites binders. Among all the IL modified carbon electrodes and IL functionalized carbon nanocomposites, the IL/graphene electrodes and IL/graphene/carbon nanocomposites showed enhanced electron transfer kinetics. This is because ILs tend to enhance the graphene dispersability leading to highly stable novel electrodes and nanocomposites^[186].

Ng *et al*^[189] prepared a 3DGR/ 1-butyl-3-methyl imidazolium hexafluorophosphate ([BMIMPF₆]) using direct mixing of the two components, i.e. they synthesized GR and then mixed it with the ionic liquid followed by grinding them together in an agate mortar for 30 minutes and this formed a black homogeneous paste. The paste was deposited on a glassy carbon electrode which had just been cleansed and coated with nafion (to remove interfering species and to prevent IL from leaking into the solution). The prepared composite was investigated by field emission scanning electron microscopy, FTIR, and electrochemical workstation (with three electrode system). The SEM images were used to differentiate between the GR and GR/IL composite, and the results revealed that the GR was a porous, loosely packed nanosheet whereas the composite had a porous, uniform structure which is attributed the π - π and π -cation interactions between GR and IL. The pores within these nanoparticles are believed to give the material a stoichiometric electron acceptance or hosting (for electron donating guest species) character. The FTIR spectra of the composite showed some peaks at; 1725, 1566, 1572 and 1263, and 837 cm⁻¹ which are due to C=O of acid moieties on GR edges, benzoid rings (of GR), C-N in imidazolium, and P-F in the IL respectively, and these indicate the successful incorporation of IL into GR structure. The electrochemical behaviour of this composite electrode shows that it has a large electroactive surface area and behaves as a combination of a thin-layer electrochemical cell and a planar disk electrode. Finally this GR/IL electrode showed sensitivity of 11.2 $\mu\text{Acm}^{-2}(\mu\text{mol L}^{-1})^{-1}$ and a detection limit of 16 nM towards NO sensing.

Guo *et al*^[186] prepared the GR/ IL (they used IL-NH₂ which is the ionic liquid that ends with NH₂) by mixing GO and IL under stirring and then followed by in situ reduction of GO using hydrazine at 80°C for two hours. The electrode of this composite was made by polishing the glassy carbon electrode with different concentrations of slurry alumina, rinsing with deionised water, sonicating in acetone and water, and finally coating it with the composite. The atomic force microscopy (AFM) image of GR/IL revealed that the composite consists of flake-like nanostructures and has an average thickness of ~1.2 nm which is a typical characteristic of functional molecule protected single layer graphene nanosheets. This thickness is due to the IL chains which are sandwiched between the graphene sheets. TEM images show the wrinkled topology of the composite which is caused by the small GR/IL thickness. The FTIR spectrum showed 2935, 2843, and 1164 cm⁻¹ peaks which are due to CH₃(N), CH₂(N) stretching, and the

asymmetric in-plane stretching of imidazolium ring. The electronic structure of GR/IL composite was studied using X-ray photoelectron spectroscopy (XPS) and the spectrum contained the dominant energy binding peaks at 284.6 eV which resulted from C-C bonding, the weak 286.7 and 287.7eV which are due to C-O bonding, the 401.7 and 399.9eV which indicate the N1s band. The above results indicate that the IL was really grafted onto the GR sheets. The prepared electrode showed a 6.2 times higher signal detection for trinitrotoluene (TNT) as compared to ionic liquid/carbon nanotube/glassy carbon electrode (IL/CNT/GCE). Over and above that, the GR/IL/GCE showed a very good reproducibility and stability for TNT detection.

2.9. CONCLUSION OF THE LITERATURE SURVEY

This chapter discussed in details the synthesis, properties, and applications of polyaniline and graphene. It pointed out the importance of constantly developing their structure and their properties. It is also important to realize the effects of the media used to the material itself and to the environment. Thus, the significance of this study is to try and develop a synthetic method which is not only environmentally friendly but which may also result in producing materials which have advanced properties.

CHAPTER3

INSTRUMENTATION AND METHODOLOGY

3.1 INTRODUCTION

The previous chapter reviewed the relevant literature concerning polyaniline, graphene and ionic liquids. Nanoparticles have enhanced properties as compared to bulk particles, these include: optical, mechanical, thermodynamic, etc. Characterization of these particles enables their fundamental studies including correlating the material's structure, shape, and size, and leading to conclusions about their physical and chemical properties. This chapter outlines the instrumental techniques used and the synthesis of the materials.

3.2. INSTRUMENTAL

For many years characterization instruments have been invented and developed to produce qualitative results. Characterization of material in this study include scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and ultraviolet visible (UV-vis) spectrometries, energy dispersive X-ray (EDAX), X-ray diffractometry (XRD) and Thermogravimetric Analysis (TGA).

3.2.1 SCANNING ELECTRON MICROSCOPY (SEM)

Electron microscopy is one of the techniques used for material characterization. These techniques use a beam of high energy particles (electrons) to illuminate a specimen and then produce an image of that specimen. Electron microscopy techniques such as scanning electron microscopy (SEM), and transmission electron microscopy (TEM) offer better resolution than optical microscopy which uses photons/visible light (these photons have less energy)^[190,191].

SEM is an electron microscope that provides the images of the specimen's external morphology by scanning a sample with the beam of electrons in a raster scan pattern. The raster pattern that is implied in scanning the sample surface means that the beam of electrons is swept across a surface in a straight line (x-direction, returned to its starting position and shifted downward (y-

direction) by a standard increment. The interactions between the atoms on the sample surface and the electron beam produce signals such as backscattered, Auger and secondary electrons, x-ray fluorescence photons, and cathodoluminescence. The produced signals provide information about the composition, electrical conductivity, topography (physical features of material surface) and other properties of the material's surface. The sample to be characterized should be electrically conductive in the solid state, or if the sample is non-conductive, it should have an ultrathin coating of a conducting material; usually a metal coat is employed, or be analyzed with a low vacuum instrument. A SEM instrument consists of electron source, condenser lens, sample chamber, objective lens, deflector, detector, and the CRT displays, figure 3.1. Typically the sample is irradiated with the electron beam, the signal (emitted electrons) is converted into an intensity modulation and then the image is displayed in a CRT display^[190,191].

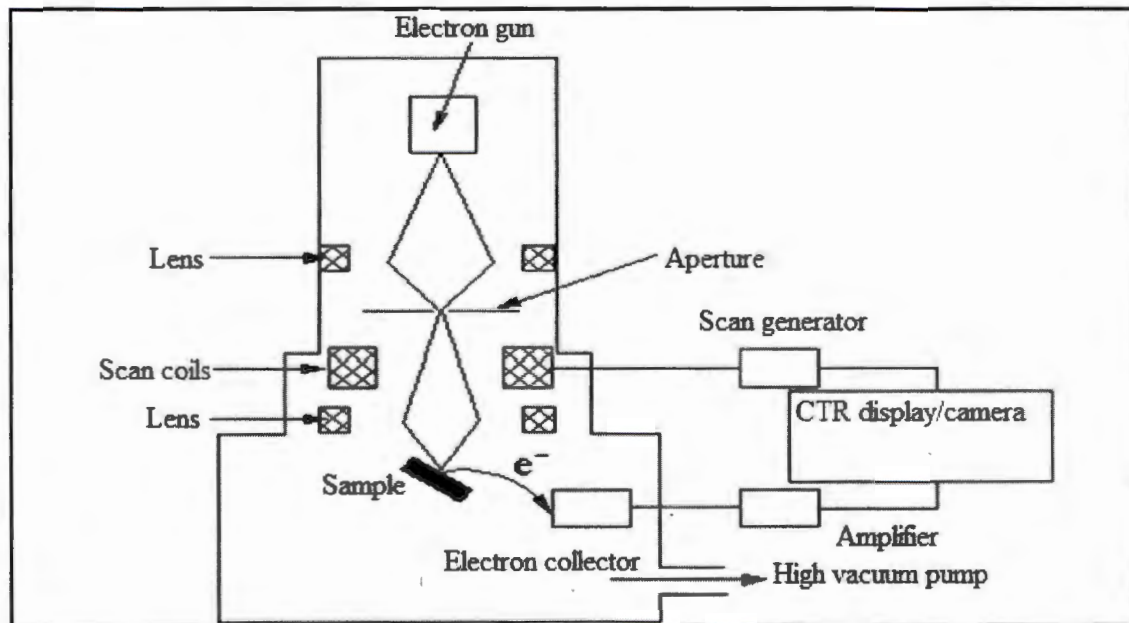


Figure 3.1: Schematic representation of SEM^[190]

3.2.2. ENERGY DISPERSIVE X-RAY DIFFRACTION ANALYSIS (EDAX)

There are two types of X-ray spectrometry and these are; the energy dispersive spectrometry, EDS (or energy dispersive X-ray diffraction analysis, EDAX) and wavelength dispersive

spectrometry, WDS. These techniques are used for measuring the energy and wavelength of the photon respectively. Both of them can be coupled in the SEM, and the EDAX could also be coupled with Transmission electron microscopy (TEM)^[191].

EDAX can be used in several industries such as the automotive, aerospace, biomedical/tech, defense (forensics), lighting, polymer and telecommunication industries for materials' elemental composition imaging and mapping of the elements present in defects. Typically EDAX could be applied in foreign metal alloy identification, corrosion evaluation, rapid material analysis, phase identification and distribution, and coating composition analysis. This technique is fast, versatile, and inexpensive^[192,193].

The instrument consists of the beam source, X-ray detector, pulse processor, and the analyzer (figure3.2). A beam of high energy incident electrons is bombarded on a sample and one of the high energy electrons excites the sample's electron from an inner shell atomic orbital. The resulting "hole" will be filled by an electron from a higher energy shell. During this transition the electron emits a photon or packet of energy which is detected as an X-ray. This energy is detected and converted to an electronic signal by the detector. The processor determines the energy of each released X-ray by measuring the electronic signal. Finally the analyzer displays and interprets the data^[191].

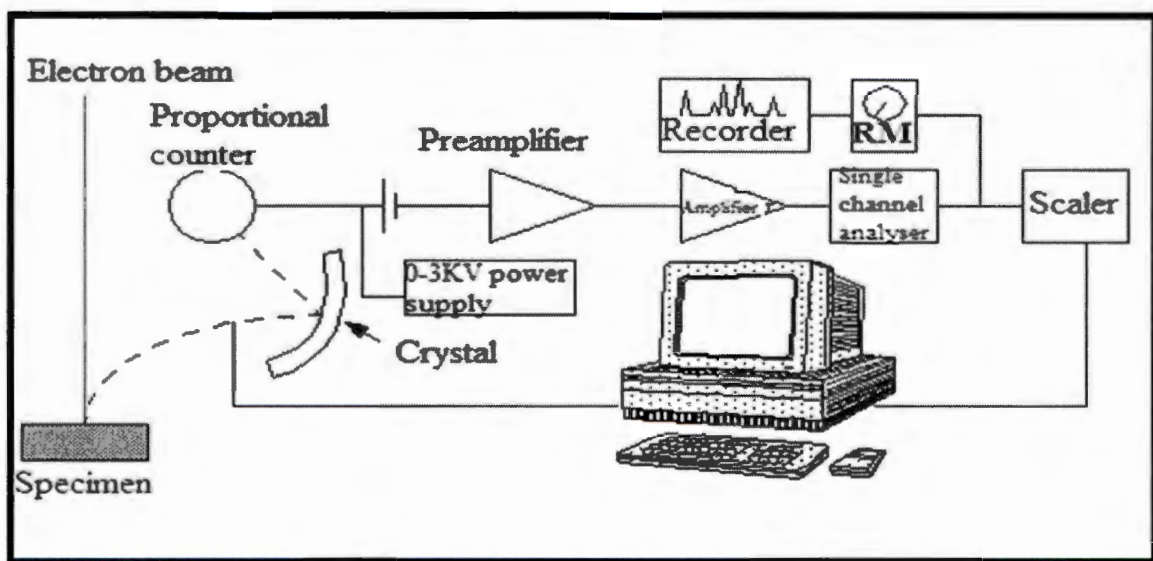


Figure 3.2: Schematic representation of EDAX

3.2.3. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

The IR light is an electromagnetic radiation which is within a wavelength between 0.78-1000 micrometers or wavenumbers from 13000-10 per centimeter (cm^{-1}). The principle behind IR spectrometry is that the sample should absorb electromagnetic radiation in the IR region, causing the vibrational excitation of bonds within the molecule. IR spectroscopy is used to obtain information on the molecular structure of the sample in all states of matter. This information output from the instrument is called the IR spectrum. The spectra could be divided into three groups, namely: far IR ($400\text{-}0\text{ cm}^{-1}$ or $25\mu\text{m}$ and beyond), mid IR ($4\text{ }000\text{-}400\text{ cm}^{-1}$ or $2.5\text{-}25\mu\text{m}$), near IR ($14\text{ }285\text{-}4\text{ }000\text{ cm}^{-1}$). Among these three regions, mid IR is the most used because it is the most accessible region^[190,194,195].

IR spectroscopy utilizes three kinds of instrumentation namely: dispersive, Fourier transform, and non-dispersive spectrometers. Fourier transform IR is widely used because of the advantages that it offers such as having Connes, Jaquinot, and Felleget advantages. Analysis of matter is carried out using either transmission or reflectance methods depending on the type and concentration of the sample under study^[190,195]. It is difficult to analyze mixtures. When analyzing aqueous samples, special cells are required^[194]. The FTIR consists of radiation source, interferometer, and detector, see figure3.3. Typically the beam of infrared light is produced, passed through an interferometer, and then split into two separate beams. One is passed through the sample; the other is passed through a reference. The beams are both reflected back towards a detector, however first they pass through a splitter, which quickly alternates which of the two beams enters the detector. The two signals are then compared and a printout is obtained^[190,195].

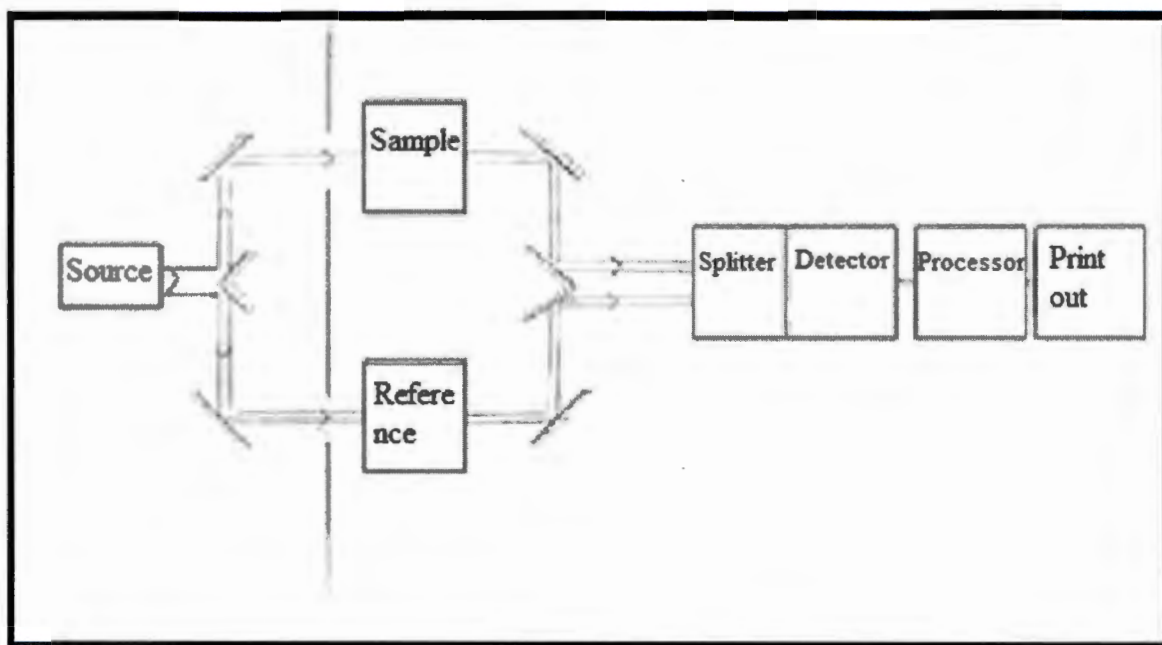


Figure 3.3: Schematic representation of FTIR double beam spectrometer

3.2.4. ULTRA VIOLET VISIBLE SPECTROSCOPY (UV-Vis)

The UV-Vis light is electromagnetic radiation which is within the wavelength region of 190-800nm. The principle behind UV-Vis spectroscopy is that the sample should absorb electromagnetic radiation in both the visible and the ultraviolet regions of the spectrum resulting in changes in the electronic structure of ions and molecules. This technique can be used in the identification and structural analysis of materials. The analyzed sample should be in a liquid form, that is solids should be dissolved, and if they are insoluble, a reflectance cell should be used ^[190,194,196].

The UV-Vis spectrometer consists of the following main components; the radiation source, a monochromator, sample cell compartment, detector, and a display (figure 3.4). The UV-Vis instrument comes in two forms; single and double-beam spectrometers. In a single beam spectrometer, the readings of a blank (reference) are taken, followed by those of a sample (that is one cell at a time is inserted in the instrument). The same principle of taking the readings of the sample and the blank is followed in the double-beam instrument, the only difference is that here the readings are taken simultaneously; because the instrument has two cell compartments. After

the release of the beam by the radiation source, the beam is split into two components and passes through the reference and sample cells at the same time^[190,196].

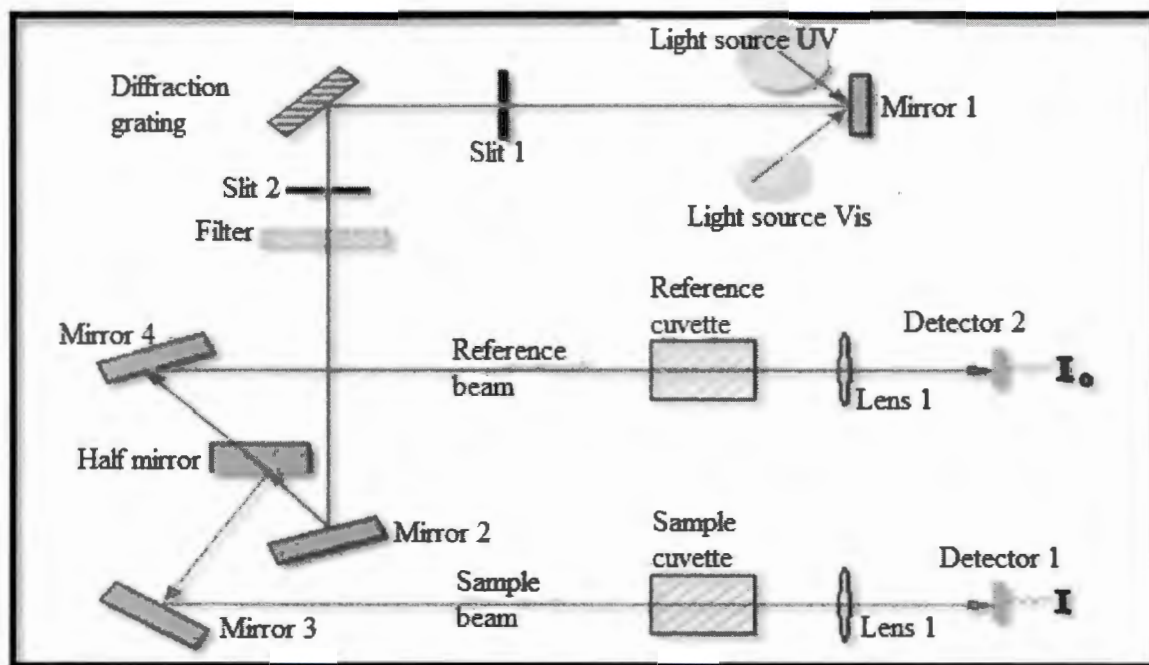


Figure 3.4: Schematic representation of a double-beam UV-visible spectrometer^[190]

3.2.5. X-RAY DIFFRACTION SPECTROSCOPY (XRD)



XRD is a technique used for chemical analysis (investigation of high/low temperature phases, phase identification, and determination of unit cell parameters of unknown materials) and measurement of the structural properties (residual strain, grain size, phase composition, texture, and structural disorder). It can also be used to examine the arrangement of atoms in amorphous materials. Crystalline materials produce sharp narrow peaks while amorphous parts of the sample produce broad peaks and the ratio between the two is used to calculate the crystallinity of the material. It can also be used to determine the thickness of multilayers and thin films. XRD methods are rapid and cheap^[190].

A typical XRD instrument consists of X-ray tube, incident beam optics, goniometer, sample holder, receiving-side optics, and detector (figure3.5). The X-rays are emitted by the X-ray

tube/generator and become conditioned by the incident beam optics. The goniometer is used to hold and move the sample holder, optics, detector, and/or tube. The conditioned X-rays strike the sample and the diffracted/scattered rays pass through the receiving-side optics to the detector where they are counted. The diffraction and diffraction pattern are better described by diffraction-interference phenomena. This means that patterns result from X-ray diffraction or scattering or from diffraction of X-rays by the processes of interference between scattered rays. The directions in which the rays are scattered depends on the factors expressed in the Bragg's law^[190,198,199].

$$n\lambda = 2d_{hkl}\sin\theta_{hkl}$$

Where: d_{hkl} is the lattice spacing (interplanar spacing of adjacent (hkl) lattice planes)

n is the integer (the order of reflection or diffraction)

θ is the angle between the atomic planes and the incident beam

λ is the incident beam wavelength

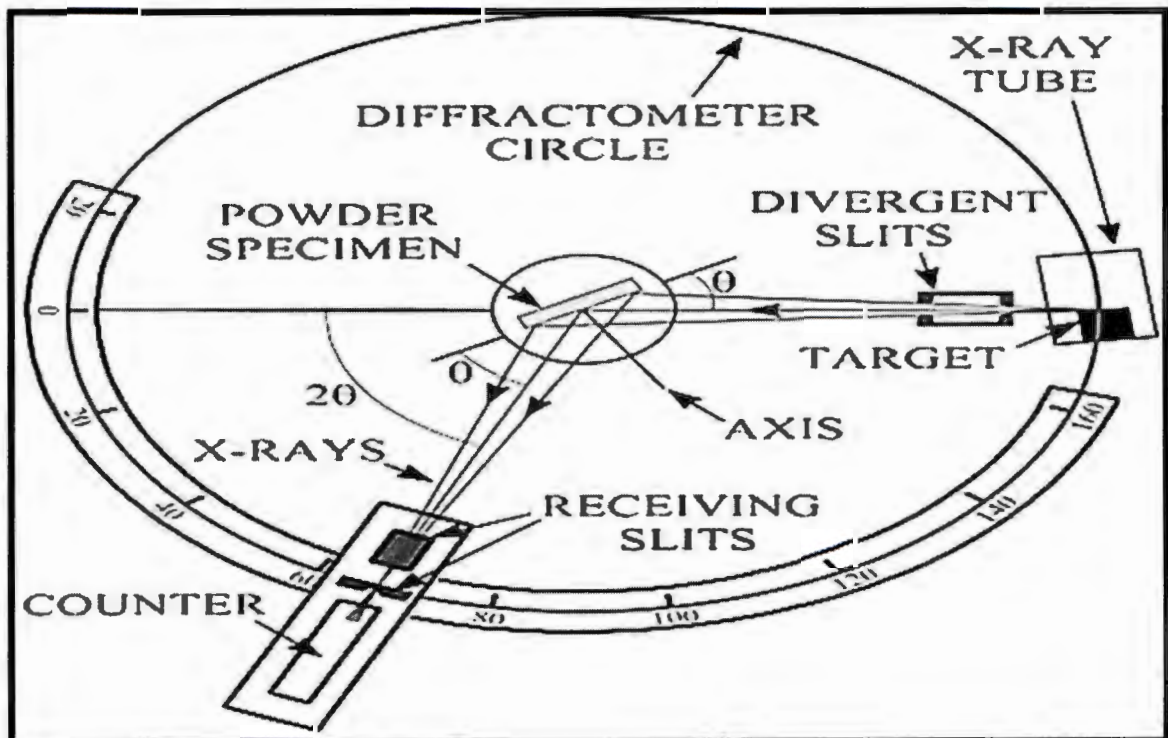


Figure 3.5: Schematic representation of XRD

3.2.6. THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermal techniques are primarily used for measuring the physical properties of matter or of the products produced after matter has undergone a chemical reaction. Among these techniques, there are those which are for chemical structure identifications. Such methods include thermogravimetric analysis (TGA), differential thermal analysis (DSC), and microthermal analysis. These techniques differ in the properties measured and the temperature programs applied^[190,200].

A thermogravimetric analysis (TGA) technique measures the weight loss of a sample as a function of temperature or time, this happens in a furnace whose temperature is controlled, and its atmosphere should be inert. The qualitative information provided by TGA is limited to oxidation decomposition reactions, and physical processes such as sublimation, desorption and vaporization. The most important applications of TGA are found in the study of polymers, identification purposes (compositional analysis and decomposition profiles) and determination of moisture content of a sample^[190,200,201].

A TGA instrument consists of a thermobalance, furnace, purge-gas system, and a computer system (figure 3.6). The thermogravimetric analysis is carried out by exponentially increasing the temperature of the furnace under an inert atmosphere. The data is then plotted as mass or mass percentage against time or temperature; this graph is called a thermogram or a thermal decomposition curve^[191,201,202]. A thermogravimetric analyzer could also be coupled with other instruments such as a mass spectrometer, or a Fourier transform infrared spectrometer^[190].

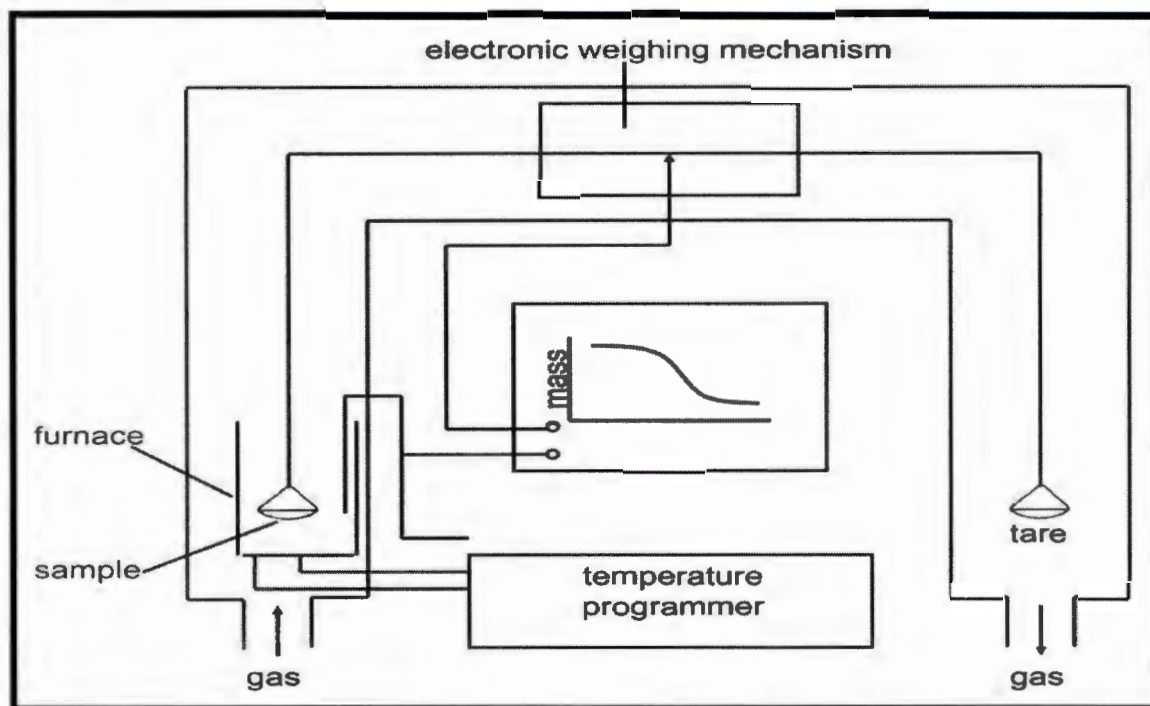


Figure 3.6: A schematic representation of TGA^[200]

3.3. METHODOLOGY

Chemical preparation of the nanostructure graphene/polyaniline was carried out by modification of the method reported by Zhang *et al*^[167].

3.3.1. PREPARATION OF POLYANILINE NANOFIBERS (PANI-F)

Polyaniline nanofibers were synthesized by a rapid mixing polymerization method. The two solutions, one made-up of hydrochloric acid and aniline hydrochloride; and the other one made-up of hydrochloric acid and ammonium peroxydisulfate, were mixed with each other under vigorous stirring for four hours. The precipitate was collected by filtration, washed with water and ethanol, and dried in a vacuum oven^[167].

3.3.2. PREPARATION OF GRAPHENE

The graphene oxide (GO) was synthesized by using the modified Hummers method. Generally, graphite and sodium nitrate were mixed and stirred in a beaker containing concentrated H_2SO_4 for 30 minutes in an ice bath. A few grams of potassium permanganate were added slowly to the suspension while under stirring. The mixture was removed from the ice bath and stirred at room temperature overnight. This was followed by addition of water and stirring of the suspension for twenty four hours while keeping the temperature at $98\text{ }^\circ\text{C}$. The following day 30% hydrogen peroxide (H_2O_2) was added to the solution, followed by purification (with 5% HCl and centrifugation) and drying. Finally the graphene was prepared by reducing GO with hydrazine monohydrate at $98\text{ }^\circ\text{C}$ ^[13].

3.3.3. PREPARATION OF GRAPHENE/POLYANILINE NANOCOMPOSITE IN DIFFERENT SOLVENTS (IONIC LIQUIDS AND CONVENTIONAL SOLVENTS)

The nanocomposites were synthesized via an in situ intercalative polymerization technique. Aniline hydrochloride was diluted in different ionic liquids or organic solvents, and GO was added into this mixture which was then sonicated for thirty minutes and stirred vigorously using a magnetic stirrer for another thirty minutes (in order to separate the GO layers), and then the procedure of synthesizing polyaniline nanofibers was followed. After washing, the composites were dried in a vacuum oven. The GO in the composite was reduced by hydrazine monohydrate at $98\text{ }^\circ\text{C}$ and the composites were washed with distilled water. This was followed by reoxidation/reprotonation of PANI-f and lastly drying.

The characterization of the nanostructured graphene/polyaniline nanocomposites were carried out using SEM, EDAX, XRD, FTIR, UV-Vis, and TGA.

3.3.4. MATERIALS

The Sigma-Aldrich materials: Graphite flake, Ammonium peroxydisulfate, 1-Butyl-3-methylimidazoliumbis(trifluoromethylsulfonyl) imide, 1-Butyl-2,3-dimethylimidazolium tetrafluoroborate

The Fluka materials: Aniline hydrochloride, 1-Butyl-3-methylimidazolium hexafluorophosphate

LAB CHEM materials: Hydrogen peroxide 30%

Merck materials: Hydrochloric acid 32%, Sulphuric acid 95-99%, Potassium permanganate ,
Sodium nitrate , Ethanol absolute, Hydrazonium hydroxide.

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CHAPTER 4

RESULTS AND DISCUSSION

4.1. INTRODUCTION

In the previous chapter the instrumentation and the chemical synthesis were discussed. This chapter gives the scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), X-ray diffractometer (XRD), fourier transform infrared spectroscopy (FTIR), ultraviolet visible spectroscopy (Uv-Vis) and thermogravimetric analysis (TGA) results. The properties of different nanosized graphene/polyaniline composites which had been synthesized in different ionic liquids and conventional solvents are then discussed.

4.2. SCANNING ELECTRON MICROSCOPY (SEM)

The morphology of graphene (GR), polyaniline (PANI), and the GR/PANI nanocomposites were studied using the scanning electron microscopy ABT60 Scanning Electron Microscope. The micrographs were taken at 1 μ m as depicted in figures 4.1-4.3.

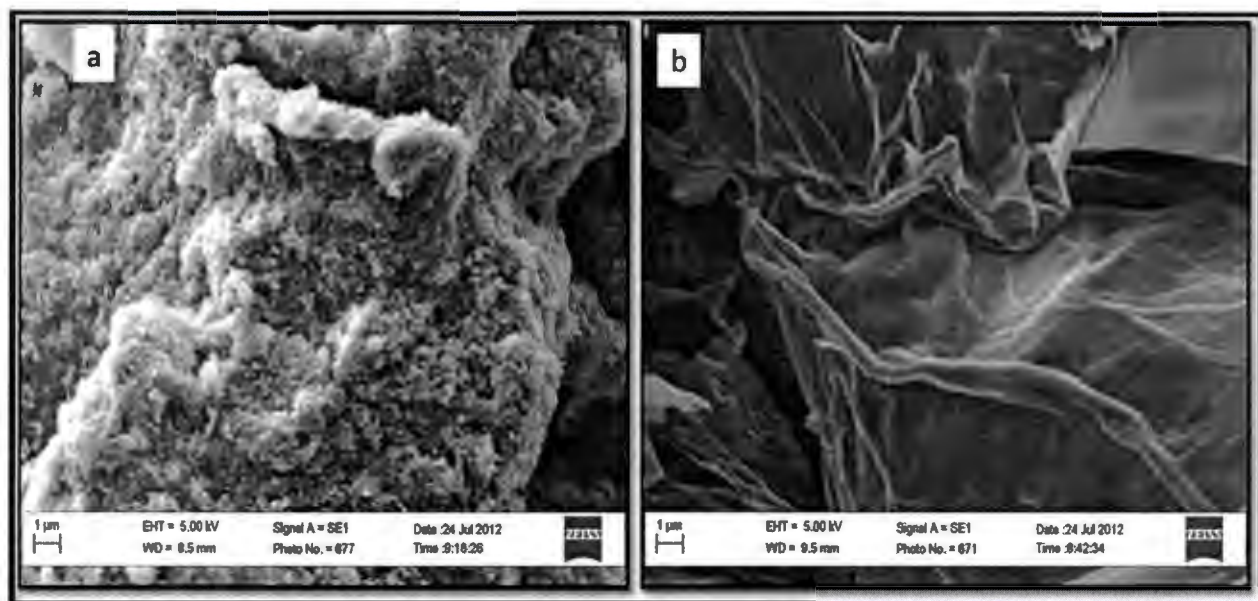


Figure 4.1: (a) The SEM micrograph of polyaniline nanofibers prepared in 1M HCl (PANI) and (b) the SEM micrograph of graphene (GR).

Figure 4.1(a) shows the SEM micrographs of PANI nanostructures which were synthesized in an aqueous solution of HCl (1M). The prepared nanostructures are in a fiber form and of course the fibers are nucleated because they were formed under vigorous stirring^[54]. Figure 4.1(b) shows the image of graphene which was reduced in water as a dispersing agent. This picture shows that graphene is wrinkled and this may have happened during the reduction because reduction of GO causes the material to form irreversible agglomerates, thus this agglomeration may have caused the thin monolayer sheets of graphite to get wrinkled^[119].

Figures 4.2(a)-4.2(e) are the scanning electron micrographs of the graphene/polyaniline nanocomposites which were synthesized in different conventional organic solvents which are toluene, dimethyl sulfoxide, dichloromethane, acetone, and tetrahydrofuran respectively.

All these solvents are polar aprotic solvents, except for toluene which is a non-polar solvent. When looking at the SEM images of GR/PANI nanocomposites, we can see that the polymer in the composite which was synthesized in toluene is well spread on the GR sheets. The polymers in the composites which were synthesized in the DMSO, acetone and THF have similar configurations, that is they look like slippery wafers or flakes. In the DMC synthesized composites, the GR sheets formed cone-like structures in which the loosely packed nanofibrillar PANI is beautifully embedded. The wafer-like PANI may have been caused by the miscibility of the solvents (DMSO, acetone, and THF) in water. During the in situ polymerization the initiator was dissolved in a diluted HCl and if the solvents are water miscible it means that there is a possibility that the new polymers will be formed on top of the pre-formed ones, and this caused agglomeration of particles^[54]. On the other hand the polymers in the composites synthesized in toluene and DMC are a bit different from the ones discussed above. This may be because the polymer was formed through interfacial polymerization which allows the polymer to be formed at the interface of the two solutions and then migrates to the organic phase after formation^[15,54,4,202]. The polymers in the toluene synthesized composites are a bit nucleated and this may be due to the solvent polarity since this is a non-polar solvent.

The GR/PANI nanocomposites were also synthesized in different imidazolium based ionic liquids. Their scanning electron micrographs show that the PANI in the composites synthesized in 1-butyl-3-methylimidazolium hexafluorophosphate (figure 4.3(a)) is embedded in the coney-

like graphene structures, while the one synthesized in 1-butyl-3-methyl imidazolium bis(trifluoromethyl sulfonyl)imide is homogeneously distributed on the GR surface figure 4.3(b). The micrographs of the composites synthesized in 1-butyl-2,3-dimethyl tetrafluoroborate and 1-butyl-3-methylimidazolium tetrafluoroborate, figures 4.3(c) and 4.3(d), we realized that the polymers within the GR sheets are very fine. These fine structures could be attributed to the borate ions present in these ionic liquids because this is only visible in the composites synthesized in them^[203].

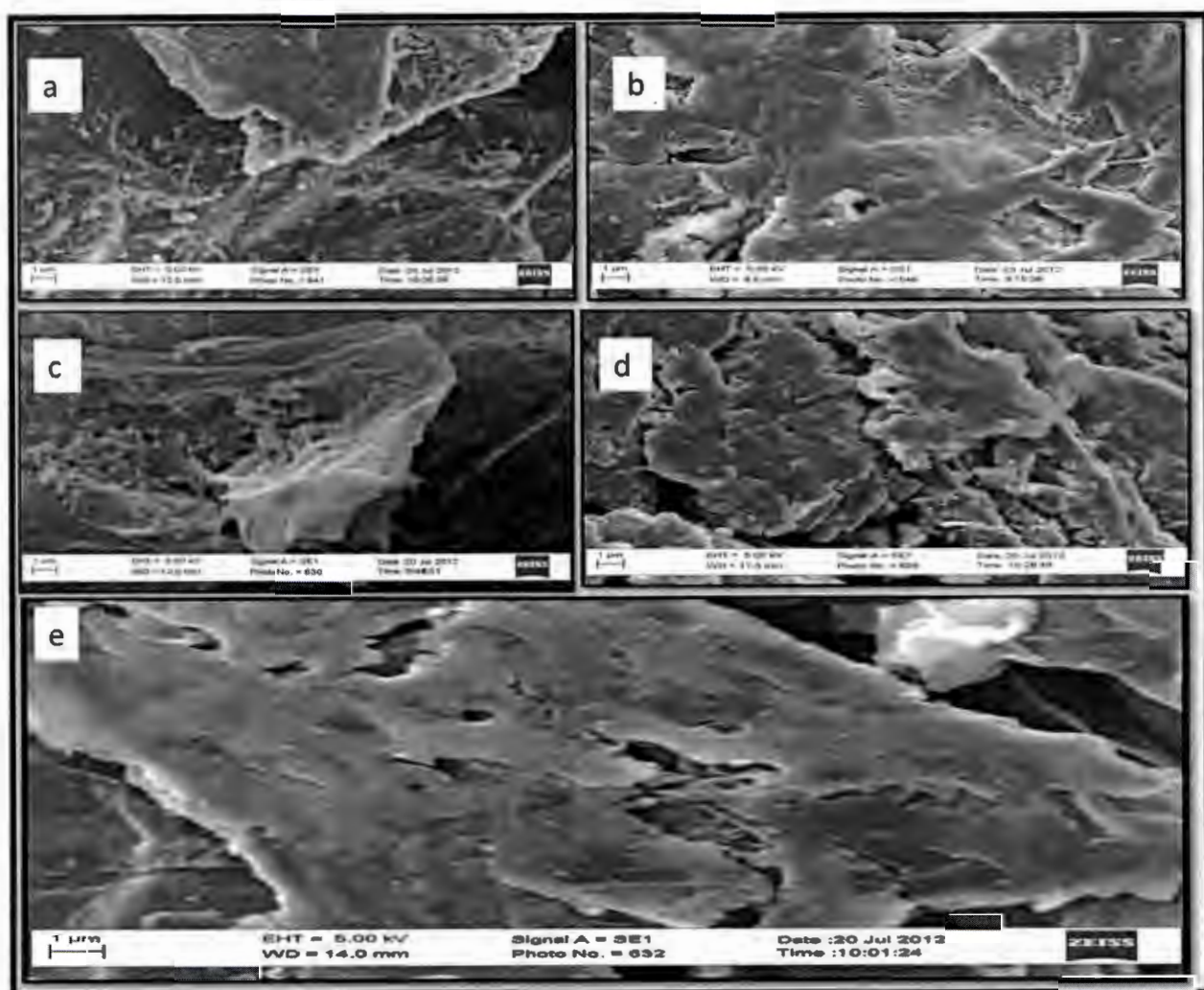


Figure 4.2: The SEM micrographs of the GR/PANI nanocomposites synthesized in organic solvents such as in (a)Toluene, (b) dimethyl sulfoxide (DMSO), (c) dichloromethane (DMC), (d)Acetone and (e)tetrahydrofuran (THF).

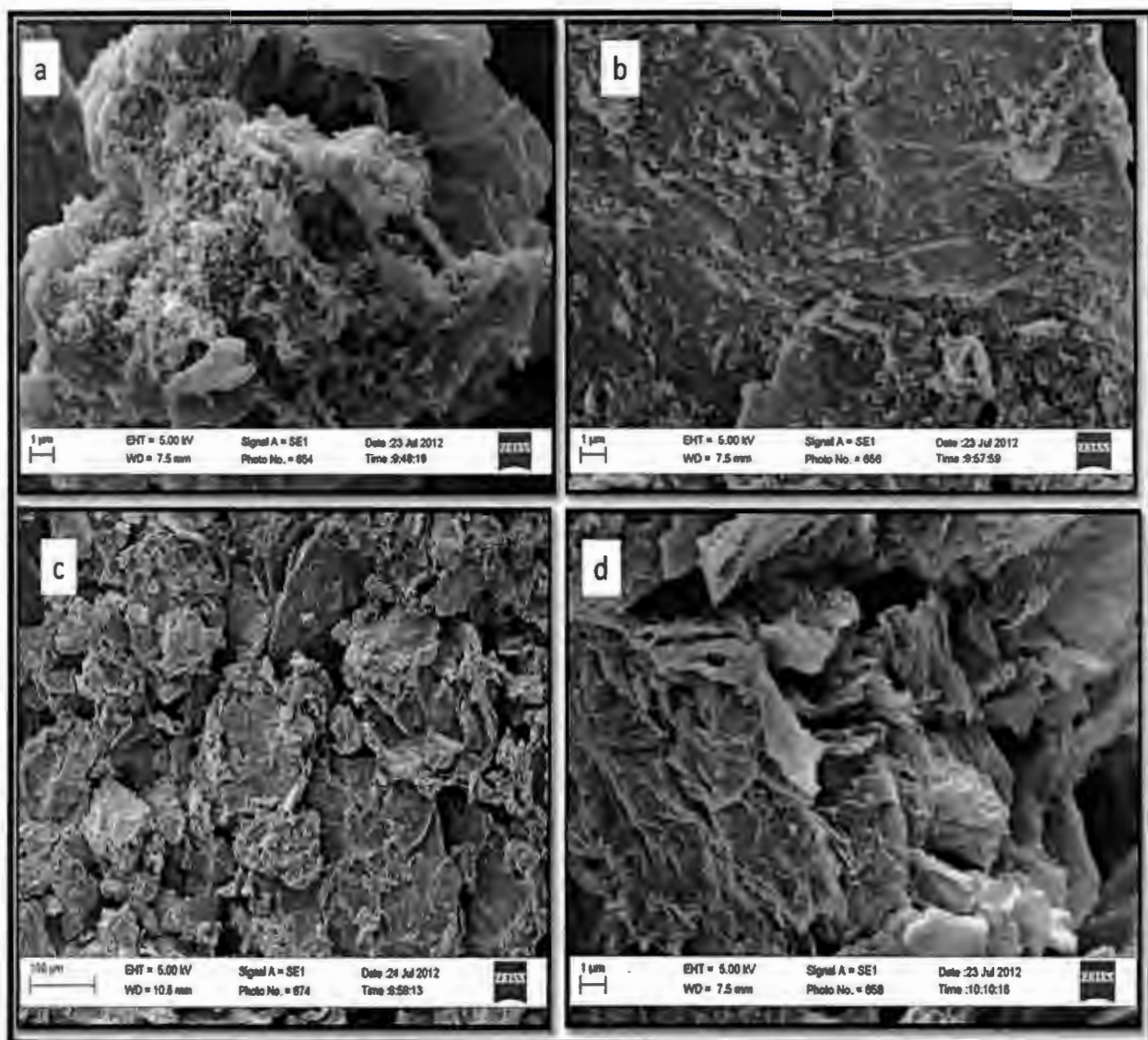


Figure 4.3: The SEM micrograph of GR/PANI synthesized in imidazolium based ionic liquids such as in (a) 1-butyl-3-methyl imidazolium hexafluorophosphate [BMIM][PF₆], (b) 1-butyl-3-methyl imidazolium bis(trifluoromethyl sulfonyl) imide [BMIM][NTF₂], (c) 1-butyl-2,3-dimethylimidazilium tetrafluoroborate [BDMIM][BF₄], and 1-butyl-3-methyl imidazolium tetrafluoroborate [BMIM][BF₄].

4.3. ENERGY DISPERSIVE X-RAY ANALYSIS (EDAX)

Energy dispersive X-ray analysis is one of the instrumental techniques which were used for characterization of our samples. The elemental X-ray analysis coupled ABT60 Scanning Electron Microscope was used for elemental analysis of the PANI, GR, and GR/PANI

nanocomposites. The following graphs illustrate the weight percentages of different elements which were present in different samples.

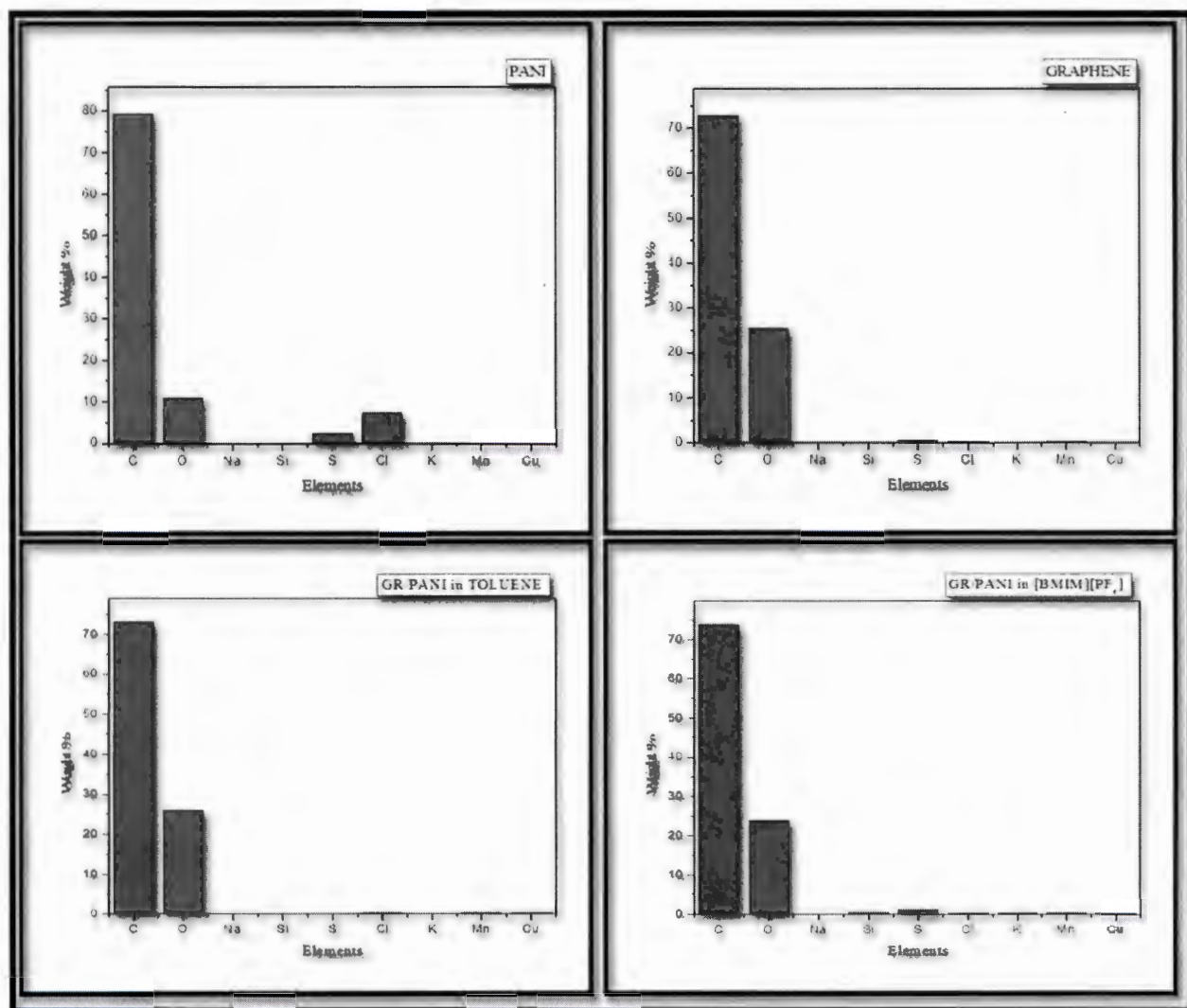


Figure 4.4: EDAX graphs of PANI, GR and of GR/PANI synthesized in toluene and [BMIM][PF₆] respectively.

Synthesis of polyaniline was achieved by polymerization of anilinechloride in an aqueous solution of 1M HCl; the process was initiated by the addition of an ammonium peroxydisulfate (APS). In theory, the constituents of this polymer should be carbon, hydrogen, nitrogen, and chlorine but the EDAX (figure 4.4) reveals that there are other elements such as oxygen and sulphur present in the sample. These items have resulted from the conversion to carbon

nanomaterials, hence the formation of carbon and oxygen. Nitrogen (N) was not detected because the instrument was run under nitrogen gas ^[167,203].

Graphene is said to be an sp^2 hybridized monolayer of carbon atoms which are arranged in a hexagonal honey-comb structure ^[167,204]. This definition means that there should not be any other elements present in the graphene sample. This could only be possible (unless otherwise a new method of reduction of GO could be invented) when thermal methods such as CVD are used to prepare graphene. The graphite flake used occurs naturally, and this means that there is a higher possibility of contamination that may be found in this starting material. The EDAX results (figure 4.4) show that the carbonyl and the hydroxyl groups of the GO were not fully reduced (this is indicated by the 25% of oxygen that is present in the resulting GR), these were born out of the oxidation of graphite stack ^[205-207].

When assessing the EDAX graphs of the graphene/polyaniline nanocomposites (figure 4.4 as well as figures 6.1-6.7 in appendix 6.1), we see that the amount of carbon atoms present in them is between 71 and 74% and that the amount of chlorine present in the samples is lower than the one in polyaniline alone. This is due to the fact that these samples were prepared using the in situ oxidative-reduction/re-oxidation-redoping process; this means that the doping degree of the polymer within the composites was decreased by the reducing agent (hydrazine hydrate) when the GO ^[167,208]. Though we tried to reoxidise and redope the PANI, high percentages of doping was not achieved. Hydrazine hydrate is a very strong reducing agent. Its addition to the GO/PANI was being reduced composites not only reduces the GO but also reduces PANI. PANI has three molecular structures which can even be differentiated physically with the naked eye using the colors associated with each of the molecular structures, and a blue color was evident after the addition of hydrazine ^[40]. This means that the emeraldine salt had been changed to emeraldine base. For this reason there was a need for further reoxidation-redoping of the composites ^[167,208].

4.4. X-RAY DIFFRACTOMETER (XRD)



The following XRD graphs were drawn using the data which were collected from irradiating the samples with X-ray light; this was carried out in a Brucker AXS-D8 advance diffractometer,

using a Cu-K α radiation with a wavelength (λ) of 1.5406Å. This technique was used for measuring both the interlayer spacings and the crystallite sizes of the samples, figures 4.5 and figure 6.8-6.14 (in appendix 6.2).

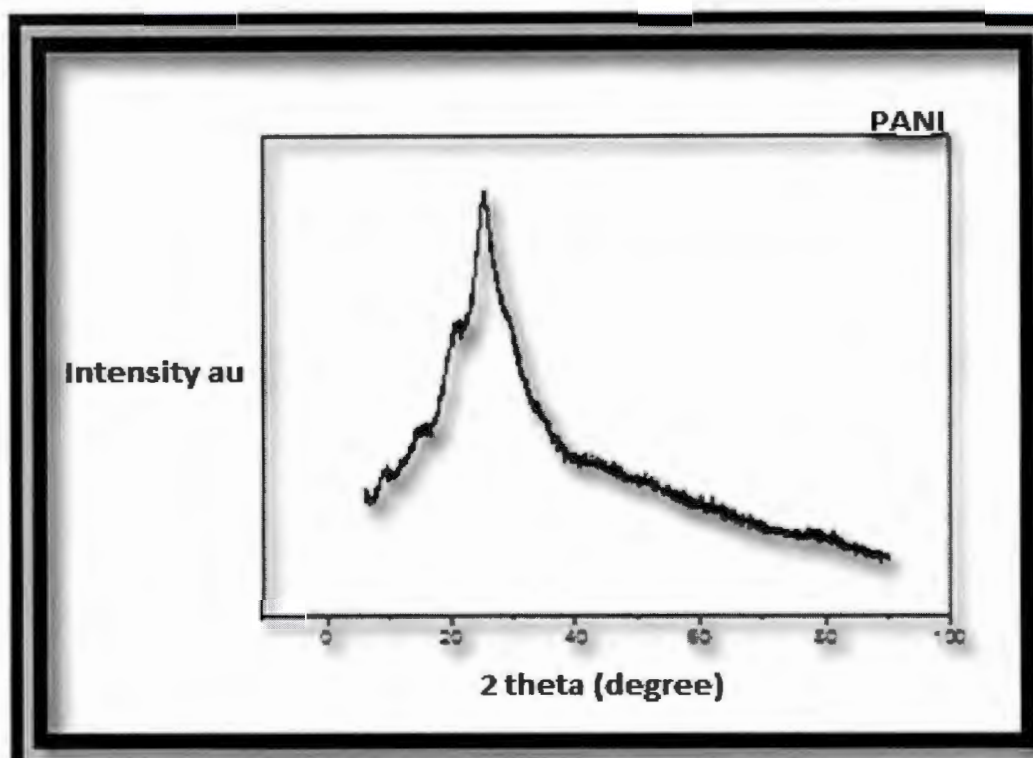


Figure 4.5 a: XRD of PANI nanocomposites

The XRD spectrum of polyaniline nanofibers shows 2 θ peaks at 9.37, 16.00, and 25.72°. According to Braggs law: $n\lambda = 2d\sin\theta$, these nanostructures have the interlayer spacing of 0.346 nm, and all these sum-up to the crystallinity of PANI (figure 4.5 a). In literature, the XRD spectrum of GO (figure 4.5 b) shows a 2 θ peak between 11.6-13.1, and these peaks which correspond to the interlayer spacing of 0.72nm^[167,204,209]. This huge spacing had been assigned to the presence of oxygen containing functional groups and the water content within the GO. In the GR that we prepared, the interlayer spacing shifted down to 0.353nm. This indicates the successful recovery of the sp² conjugated carbon atoms and the crystallinity of GR^[167,204]. The 2 θ peaks at 12.09° indicates that the GR is not fully reduced and this is in agreement with the EDAX results. The 2 θ at ~25.06 and 42.9° indicate the graphite-like structures^[204].

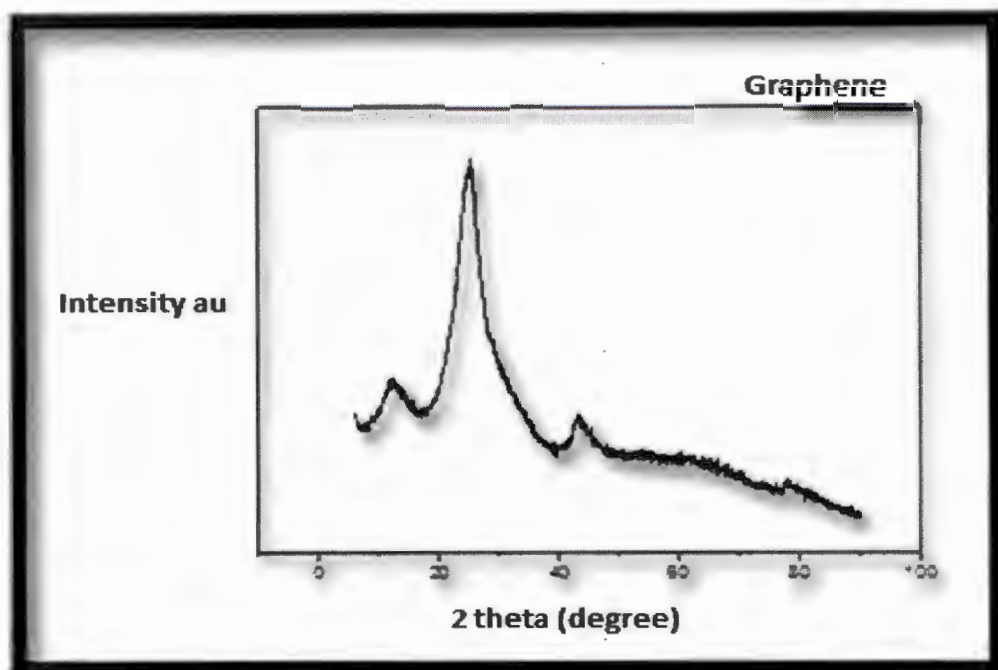


Figure 4.5 b: XRD of GR nanocomposites

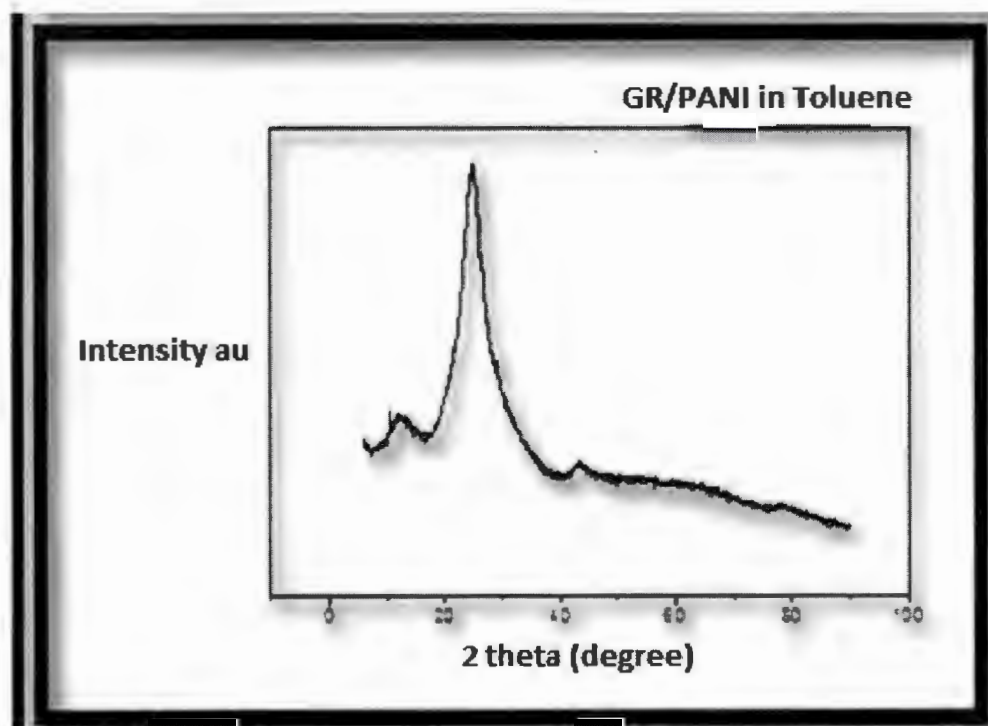


Figure 4.5 c: XRD of GR/PANI nanocomposites synthesized in toluene

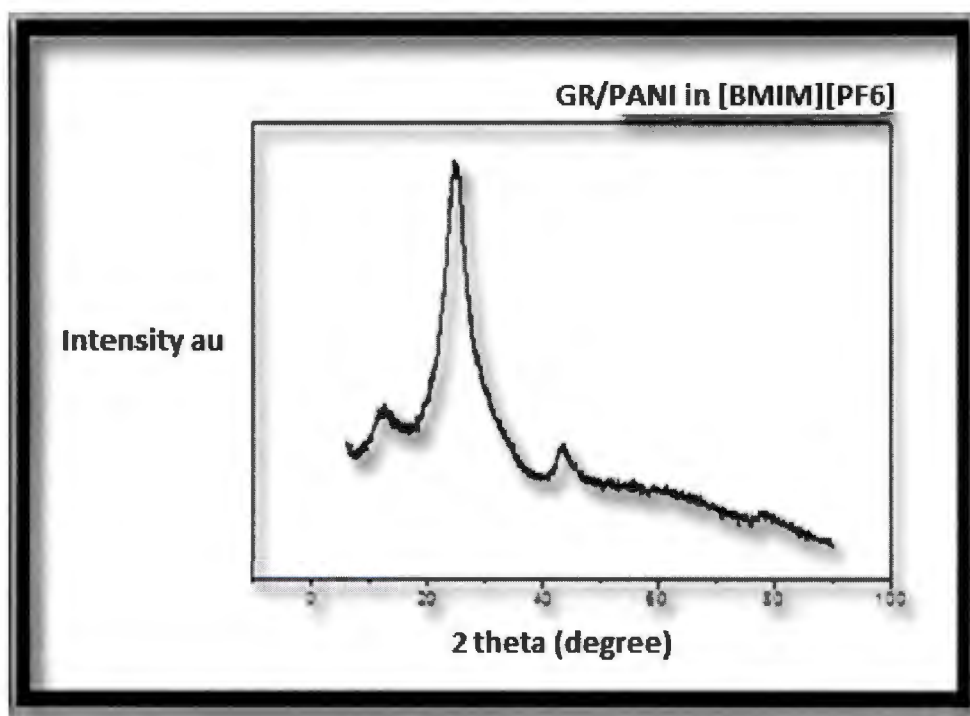


Figure 4.5 d: XRD of GR/PANI nanocomposites synthesized in [BMIM][PF₆]

The XRD spectra of the GR/PANI (figure 4.5 c and figure 4.5 d) nanocomposites show interlayer spacing ranging from 0.355-0.360 nm (Table 4.1). The peaks of these composites which are similar to those of PANI (the 16.00 and 24°) indicate the interaction between the graphene and polyaniline but the 2θ~43° could be correlated to the reduced PANI, that is PANI was in the form of a conducting emeraldine salt and after reduction by hydrazine monohydrate it changed to the insulating emeraldine base^[209]. These results are in good agreement with those obtained from the EDAX; the weight percentage of chlorine present in the composites is too low and this indicates that a higher redoping degree was not achieved.

Furthermore, XRD patterns were used to determine the crystallite size of samples using the Scherrer's equation^[210,211]:

$$T = K \lambda / (\beta \cos \theta)$$

Where: T → Crystallite size (nm)

K → Shape factor for an average crystallite (0.9)

λ → XRD wavelength (nm)

β → Width at half maximum of crystallite peak (radians)

θ → Bragg's equation.

The most intense peaks were used to calculate the crystallite size (T), see Table 4.1. The crystallite size of GR was found to 3.85 nm which corresponds to the value reported in the literature^[210,212]. In case of the PANI nanostructures the crystallite size was found to be 60.26 nm^[211]. The GR/PANI composites have the crystal size which range from ~29 to ~250 nm depending on the solvent used. When comparing the crystallite sizes of the composites synthesized in organic solvents to those synthesized in ionic liquids, it was found that those synthesized in ionic liquids have bigger values and the crystallite size values of the composites also differ. This might be due to two factors; (i) the size of PANI embedded in between the graphitic monolayers i.e. SEM showed finer structure [BF₄]⁻ anions, hence the smaller crystallite size as compared to other ionic liquids (ii) the sizes of ionic liquid anions and functional groups of ionic liquids might have influenced the crystallite size. FTIR results indicate that these anions or functional groups are present within the composites: for example the -SO₃H (sulfonic acid) is very big and it might have caused the crystallite size to be big since it is present in the composite.

Table 4.1: XRD data used for calculating the interlayer spacing and crystallite size of different samples.

COMPOUND	2 θ	θ	$d=n\lambda/(2\sin\theta)$	$T=K\lambda/(\beta\cos\theta)$
GR	25.2415	12.62075	0.353	3.854
PANI	25.7237	12.86185	0.346	60.262
GR/PANI in Toluene	24.7593	12.37965	0.359	43.500
GR/PANI in DMSO	24.88557	12.42779	0.358	29.765
GR/PANI in DMC	24.6628	12.33140	0.360	31.056
GR/PANI in Acetone	24.9039	12.42785	0.358	29.890
GR/PANI in THF	24.9039	12.45195	0.357	30.535
GR/PANI in [BMIM][PF ₆]	24.6628	12.33140	0.361	253.436
GR/PANI in [BMIM][NTF ₂]	24.9039	12.45195	0.357	946.600
GR/PANI in [BDMIM][BF ₄]	25.0968	12.54840	0.355	89.335
GR/PANI in [BMIM][BF ₄]	25.004	12.50020	0.356	89.319

4.4. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)



The Agilent Resolution Pro Carry 600 Series Fourier Transform Infrared Spectrometer was used for structural characterization of GO, GR, PANI and GR/PANI nanocomposites in a powder form. The samples were run in the wavelength range between 400 and 4000 cm^{-1} . The FTIR spectrum of graphene oxide (GO) is shown in figure 6.15 (in appendix 6.3). Theoretically, graphene oxide consists of oxygen moieties such as hydroxyl, epoxy (which are located on the sp^3 carbons in the basal plane), carboxyl and carbonyl (located on the sp^2 carbons) groups^[213,214]. As a result of these functional groups, the GO spectrum shows peaks around 1700, 1279.352, 1056 cm^{-1} which are due to the C=O, and C-O respectively, the 3300 cm^{-1} which is due to the O-H, the 1650-1450 cm^{-1} peaks are due to the C=C in benzene ring, and lastly the C-H stretch band near the 3000 cm^{-1} ^[167,215-219] (see Table 4.2 for the exact wavelength values).

Graphene is defined as a two dimensional honey comb structure of sp^2 carbon^[167,204]. This definition gives the impression that there should be no other functional groups found in the structure of graphene, but this would only be true if the graphene was produced using bottom-up

synthetic methods^[205-207]. In this study, the top-down method was used, which involved synthesizing GO and reducing it with hydrazine monohydrate. The advantage of using the hydrazine as a reductant is that it does not react with the water which was used as a medium of reaction. The disadvantage is that hydrazine is incapable of removing all the oxygen moieties which are located on the edges of the graphene (carbonyl and the carboxyl groups), therefore small quantities of oxygen moieties were found in the graphene and graphene containing samples^[118,217].

In the GR FTIR spectrum figure 4.5 a (also see Table 4.1), the epoxy and hydroxyl groups diminished after deoxygenating the GO with hydrazine monohydrate. The 1649.991 cm^{-1} peak was then seen, which was due to the C=C vibrations in the phenyl structure, and still had some peaks which were visible in the GO. Such peaks are the 1712.921 and 1261.349 cm^{-1} which were caused by C=O of COOH and C-O of C-OC/C-O-H groups respectively (this is because hydrazine is incapable of reducing these moieties)^[217].

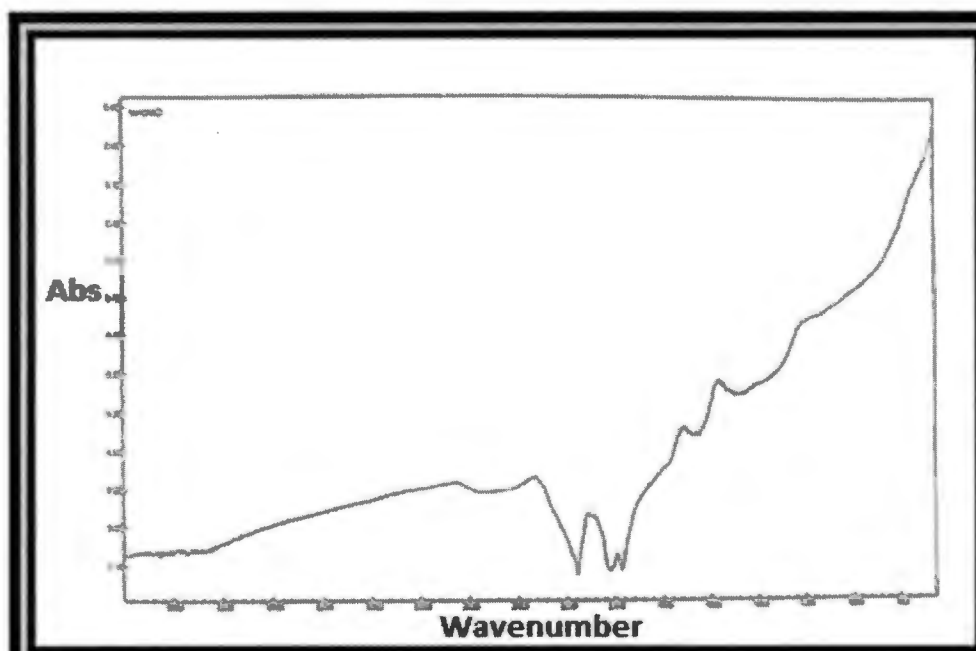


Figure 4.6 a: FTIR graph of GR nanocomposites

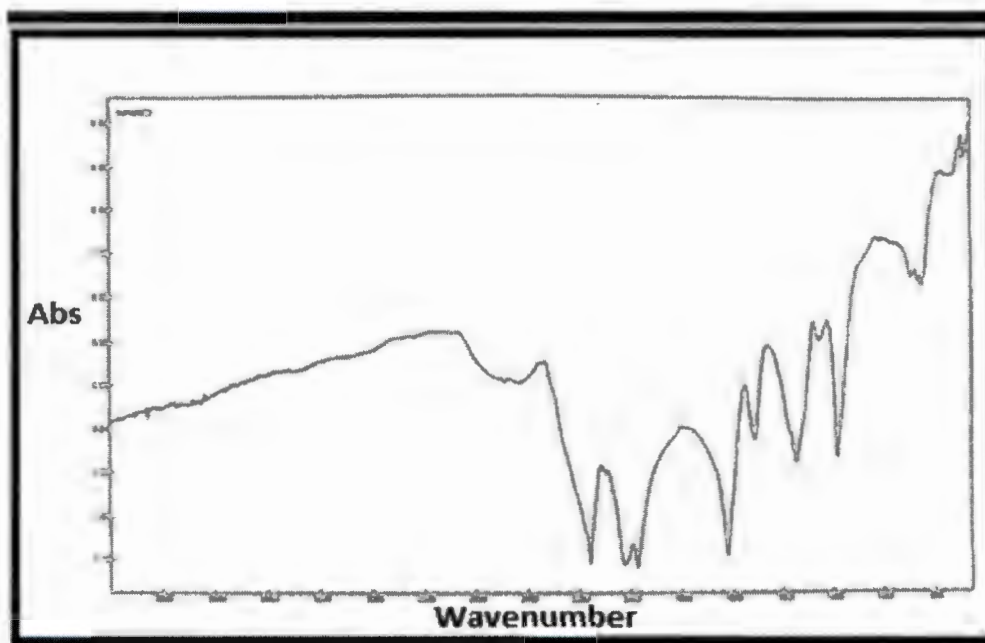


Figure 4.6 b: FTIR graph of PANI nanocomposites

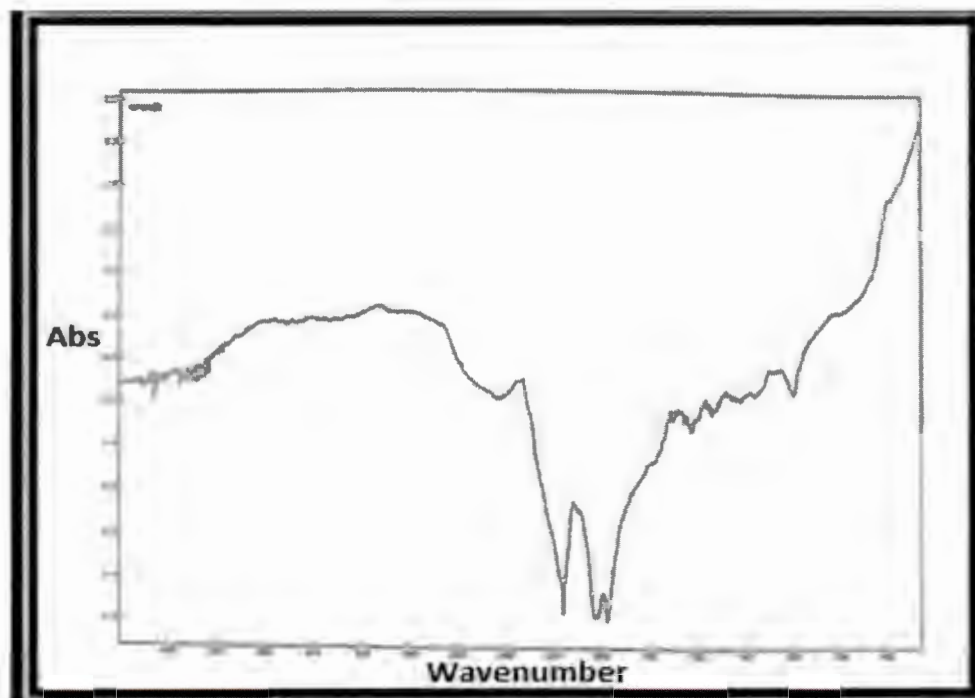


Figure 4.6 c: FTIR graph of GR/PANI nanocomposites synthesized in toluene

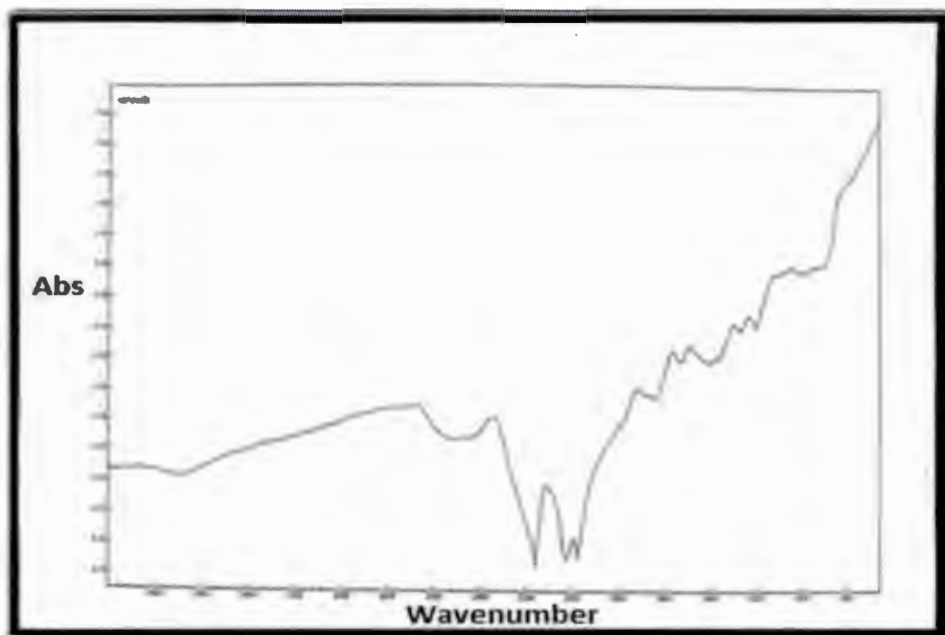


Figure 4.6 d: FTIR graph of GR/PANI nanocomposites synthesized in [BMIM][PF₆]

The vibrational modes of polyaniline emeraldine salt (PANI) were also investigated using FTIR, figure 4.5 b (Table 4.1). Some typical peaks of PANI are found around 1500, 1600, 1300, 1100, and 800 cm⁻¹, the peaks are caused by the benzoid C=C, quinoidal C=C, C-N of secondary amine stretch, C-H in-plane bending and C-H out of plane bending respectively^[49,54,167,216,219,220,221].

Polyaniline was engrafted onto the surface of graphene by insitu polymerization to make nanocomposites. Their structures were elucidated using the FTIR spectra, figures 4.5 (c and d) 6.16-6.22 in appendix 6.3 (see Table 4.2 for tabulated spectral data). Basically, the composites of graphene/polyaniline are characterized by showing peaks at ~ 1600 , 1400 , 1300 , and 800 cm^{-1} which are attributed to the C=C, C-N and lastly C-H out of plane vibrations respectively^[49,167,216,217,220-222]. The GR/PANI nanocomposites showed the FTIR peaks which slightly shifted from those of PANI and this could be due to two reasons (i) there is hydrogen bonding between the PANI backbone and the O=C-O of GR and (ii) the $\pi-\pi$ interaction between the two constituents of the nanocomposites^[216,217,220,221].

The IR spectra of nanocomposites that were synthesized in the presence of ionic liquids showed some extra peaks. In the [BMIM][PF₆] synthesized composites there is a peak $\sim 970\text{ cm}^{-1}$ which is attributed to the vibrations of the [PF₆]⁻ anion^[223] (figure 4.5(d)), around 1220 and 1070 cm^{-1} there are peaks which could be ascribed to -SO₃H in the GR/PANI composites which was synthesized in the [BMIM][NTF₂]^[219] (figures 6.20, appendix 6.3) and lastly there are the vibration modes of [BF₄]⁻ anion around 1040 cm^{-1} in the composites which were synthesized in [BDMIM] and [BMIM][BF₄]^[223] (figures 6.21 and 6.22 respectively, appendix 6.3).

Table 4.2: The FTIR spectral data for GO, GR, PANI and GR/PANI composites

Compound	Wavenumber (cm ⁻¹)	Assignment
GO	1701.114	C=O of COOH
	1272.962	C-O of C-O-C/C-OH
	3372.186	O-H of COOH & intercalated H ₂ O
	1649.991	C=C of benzene ring
	2915.277	C-H stretch
GR	1649.991	C=C of Phenyl stretch
	1712.921	C=O of COOH
	1261.349	C-O of C-O-C/C-OH
PANI	1621.235	C=C of quinoid stretch
	1515.794	C=C of benzoid Stretch
	1352.841	C-N of secondary amine
	1193.082	C-H in-plane bending
	841.614	C-H out of plane bending
GR/PANI nanocomposites synthesized in toluene	1618.040	C=C of quinoid ring
	1538.573	C=C of benzoid ring
	1349.646	C-N of secondary amine
	1289.397	C=N (-N=Quinoid=N-)
	1196.278	C-H in-plane bending
	771.320	C-H out of plane bending
GR/PANI nanocomposites synthesized in DMSO	1627.625	C=C of quinoid ring
	1528.573	C=C of benzoid ring
	1365.621	C-N of secondary amine
	1279.352	C=N (-N=Quinoid=N-)
	1196.278	C-H in-plane bending
	865.873	C-H out of plane bending
GR/PANI nanocomposites synthesized in DMC	1621.235	C=C of quinoid ring
	1522.185	C=C of benzoid ring
	1356.036	C-N of secondary amine
	1266.571	C=N (-N=Quinoid=N-)
	1193.082	C-H in-plane bending
	889.541	C-H out of plane bending
GR/PANI nanocomposites synthesized in Acetone	1624.430	C=C of quinoid ring
	1525.380	C=C of benzoid ring
	1362.426	C-N of secondary amine
	1266.571	C=N (-N=Quinoid=N-)
	1199.473	C-H in-plane bending
	879.956	C-H out of plane bending
GR/PANI nanocomposites synthesized in THF	1624.430	C=C of quinoid ring
	1522.185	C=C of benzoid ring
	1359.231	C-N of secondary amine
	1272.962	C=N (-N=Quinoid=N-)
	1196.278	C-H in-plane bending
	892.737	C-H out of plane bending

Table 4.1 Continued....

Compound	Wavenumber (cm ⁻¹)	Assignment
GR/PANI nanocomposites synthesized in [BMIM][PF ₆]	1624.430	C=C of quinoid ring
	1522.185	C=C of benzoid ring
	1359.231	C-N of secondary amine
	1263.376	C=N (-N=Quinoid=N-)
	1193.082	C-H in-plane bending
	812.582	C-H out of plane bending
	896.726	[PF ₆] ⁻ vibrations
GR/PANI nanocomposites synthesized in [BMIM][NTF ₂]	1639.997	C=C of quinoid ring
	1522.185	C=C of benzoid ring
	1365.621	C-N of secondary amine
	1221.839	C=N (-N=Quinoid=N-)
	1163.181	C-H in-plane bending
	809.777	C-H out of plane bending
	1071.666/1221.839	-SO ₃ H
GR/PANI nanocomposites synthesized in [BDMIM][BF ₄]	1621.235	C=C of quinoid ring
	1522.235	C=C of benzoid ring
	1359.231	C-N of secondary amine
	1266.959	C=N (-N=Quinoid=N-)
	1193.082	C-H in-plane bending
	865.873	C-H out of plane bending
	1090.257	[BF ₄] ⁻ vibrations
GR/PANI nanocomposites synthesized in [BMIM][BF ₄]	1627.625	C=C of quinoid ring
	1519.390	C=C of benzoid ring
	1381.955	C-N of secondary amine
	1261.349	C=N (-N=Quinoid=N-)
	1199.473	C-H in-plane bending
	865.813	C-H out of plane bending
	1076.999	[BF ₄] ⁻ vibrations

4.5. ULTRA VIOLET VISIBLE SPECTROSCOPY (UV-Vis)

The UV-vis spectra were recorded on a Perkin Elmer Lamdab750 S UV/vis spectrometer using the KBr dispersed samples. This was done within the wavelength region of 100 to 1000 nm. Graphene oxide (figure 4.7 a) is characterized by having the 223.55 and 256.87 nm UV-vis peaks which are attributed to the $\pi \rightarrow \pi^*$ transition of the aromatic C-C bonds and the $n \rightarrow \pi^*$ transition of the C=O bonds respectively^[216,218], figure 6.23 (appendix 6.4). After deoxygenation by hydrazine, the 256.87 nm peak shifted to higher wavelength (269.83 nm) and this is caused by the electronic configuration within the graphene i.e. it is due to the $n \rightarrow \pi^*$ transition of C-O bonds embedded by exfoliation and intercalation on GR^[218], figure 4.7.

UV-visible spectroscopy is one of the most important techniques in the elucidation of the structural properties of the nanostructured conductive polymers. The bathochromic shifts that are encountered in these polymers show that the energy gap of the nanosized conductive polymers is smaller than that of conventional conducting polymers therefore the nanosized polymers have higher conductivity. These could be related to the extended conjugation which is found in nanosized conductive polymer as there is an increased number of polarons in between the electronic bands^[49].

Figure 4.7 b shows the UV-Vis spectrum of PANI which has absorption peaks at 313.33, 461.41 and 843.64 nm which are attributed to the $\pi \rightarrow \pi^*$ electronic transition of benzoid rings, polaron $\rightarrow \pi^*$ and $\pi \rightarrow$ polaron electronic transitions respectively^[216,217,221,222]. The first two peaks indicate the protonation of the PANI backbone while the last one indicates that PANI is in the conductive state that is the emeraldine salt^[222].

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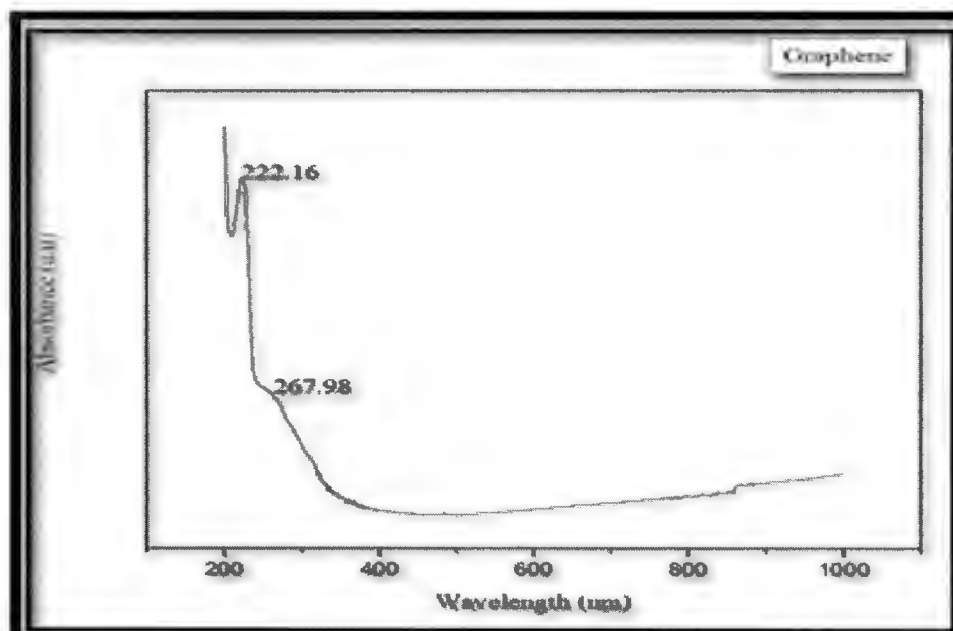


Figure 4.7 a: UV-Vis of GR nanocomposites

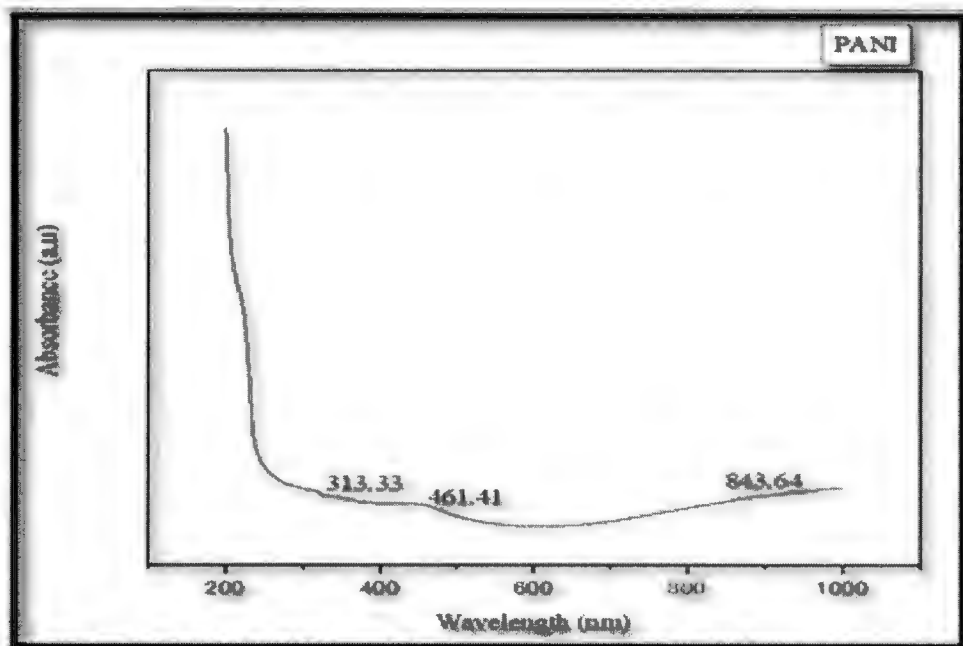


Figure 4.7 b: UV-Vis of PANI nanocomposites

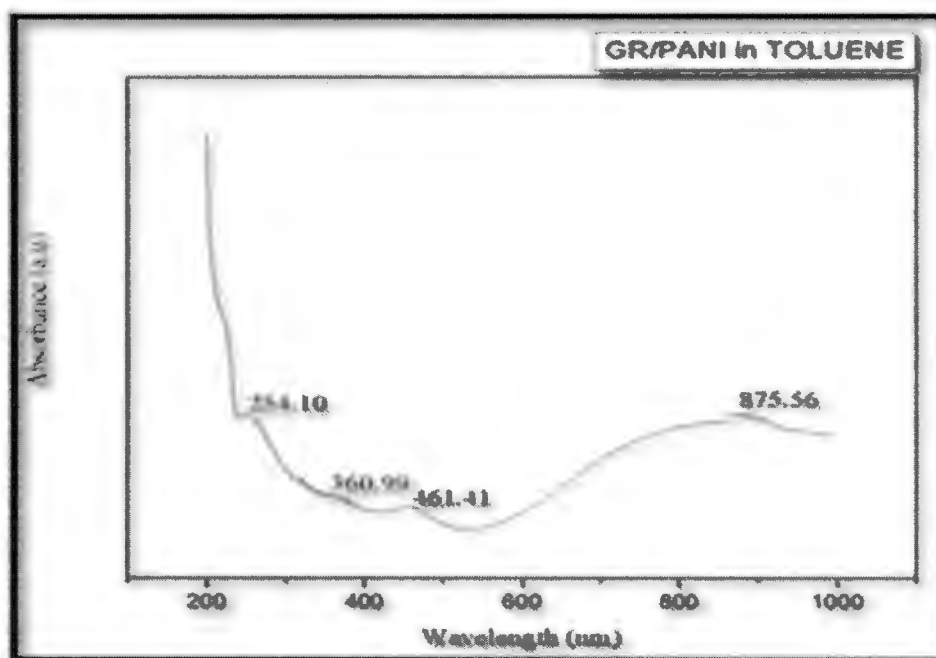


Figure 4.7 c: UV-Vis of GR/PANI nanocomposites synthesized in toluene

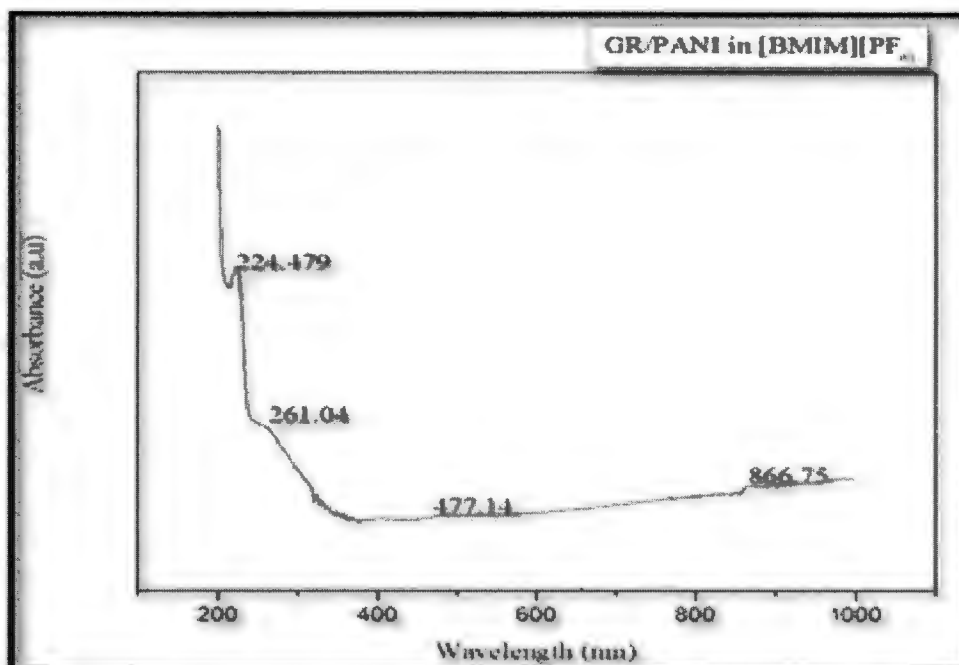


Figure 4.7 d: UV-Vis of GR/PANI nanocomposites synthesized in [BMIM][PF₆]

The composites of the graphene and polyaniline have absorption peaks which correspond to the peak characteristics of both constituents (figures 4.7 c, 4.7 d and 6.24-6.30 (in appendix 6.4)). These peaks are found ~200 nm which correspond to the $\pi \rightarrow \pi^*$ transition in the aromatic C-C of GR and ~300, 400 and 800 nm which are ascribed to the $\pi \rightarrow \pi^*$, polaron $\rightarrow \pi^*$ and $\pi \rightarrow$ polaron transitions in PANI respectively. The interaction between GR and PANI is illustrated by the shifting (slight) of the 200 nm peak towards higher wavelengths ^[215,217,221]. The presence of the $\pi \rightarrow$ polaron transitions peak in nanocomposites confirms that even though PANI was exposed to hydrazine during reduction of GO, the conductive form of PANI was recovered through the reoxidation/redoping processes. These UV-Vis results are in agreement with those of EDAX and FTIR.

4.2.6. THERMOGRAVIMETRIC ANALYSIS (TGA)

Lastly, the structural characteristics of GO, GR, PANI and GR/PANI nanocomposites were studied by thermal studies using the TA TGA Q500 thermogravimetric analyzing instrument. The samples were heated from 0 to 900 °C at the heating rate of 10 °C/min and under nitrogen atmosphere (60ml/min flow) using the ramp method.

The TGA graph of GO, (figure 6.31 in appendix 6.5) indicates that there is a small loss of weight at ~ 100°C which can be correlated to the loss of intercalated water^[167]. There is also a substantial weight loss starting from ~200 to 700°C and this is attributed to the decomposition of all oxygen containing groups i.e. the pyrolysis of -OH, -CO and -COO groups^[167,224,225]. The presence of these functional groups makes GO to be thermally unstable^[225].

Figures 4.8 a-d shows the TGA graphs of GR, PANI and GR/PANI nanocomposites synthesized in the presence of toluene and [BMIM][PF₆]. The material produced by reduction of GO at 98 °C by hydrazine (GR), lost some intercalation water around 100 °C and again there was another small weight loss from 100-600°C. This small weight loss indicates that most of the oxygen moieties were removed during deoxygenation of GO ^[167]. This is in agreement with the EDAX, FTIR and UV-Vis results which indicate that not all oxygen functional groups were removed during reduction.

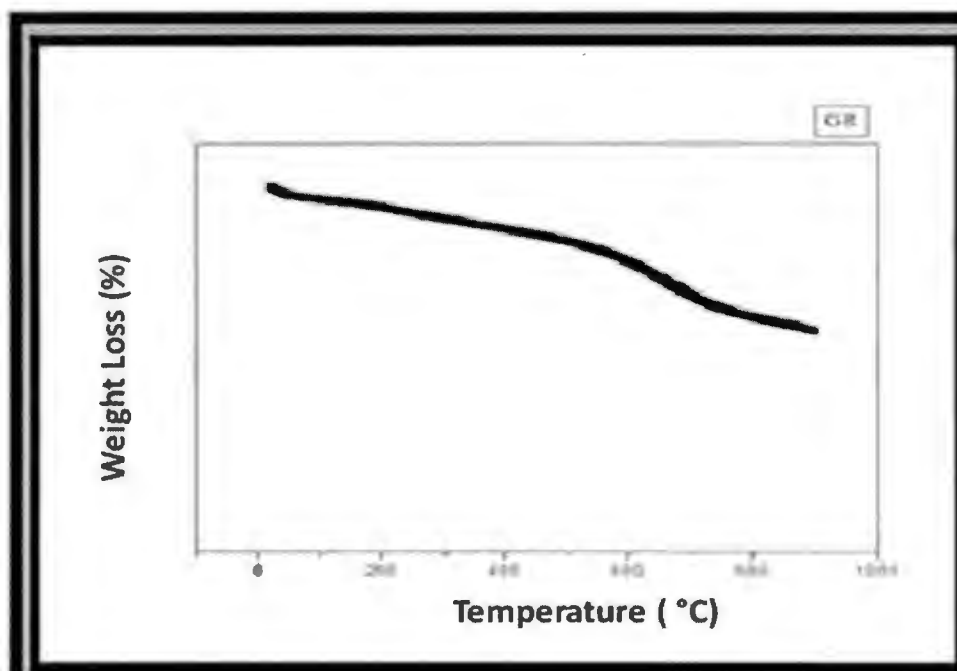


Figure 4.8 a: TGA graph of GR nanocomposites

Polyaniline undergoes thermal decomposition at around 100, 180-400 and 650-750 °C (figure 4.8 b), these mass losses are caused by removal of water and absorbed moisture in the polymer backbone, loss of dopant ions in the form of HCl(g) and oligomers, and finally the low molecular fragments and degradation and decomposition of the polymer itself^[226,227].

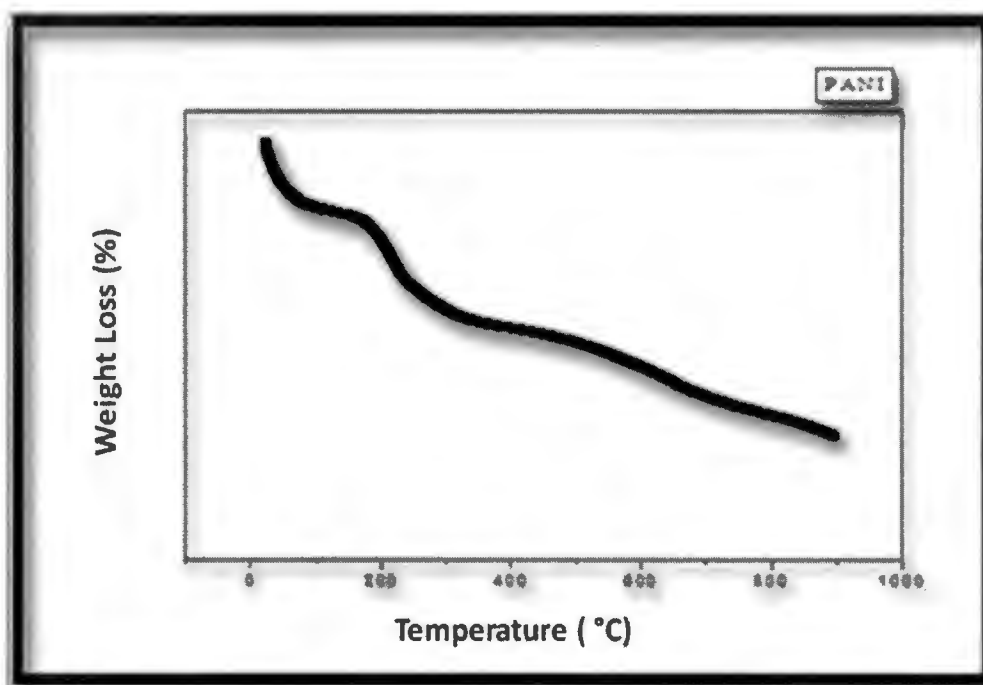


Figure 4.8 b: TGA graph of PANI nanocomposites

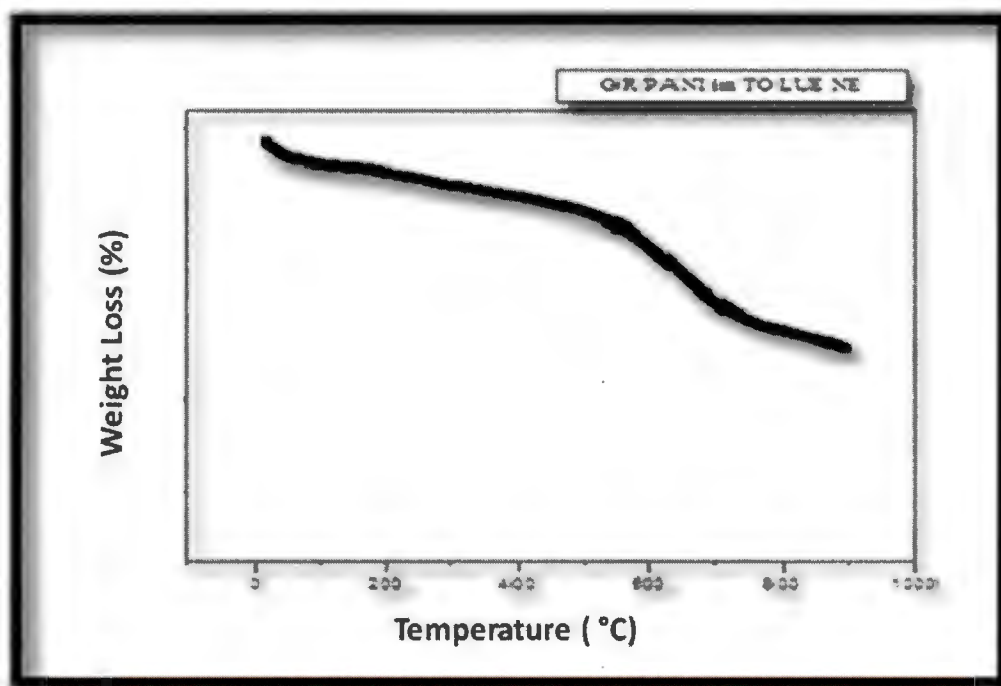


Figure 4.8 c: TGA graph of GR/PANI nanocomposites in toluene

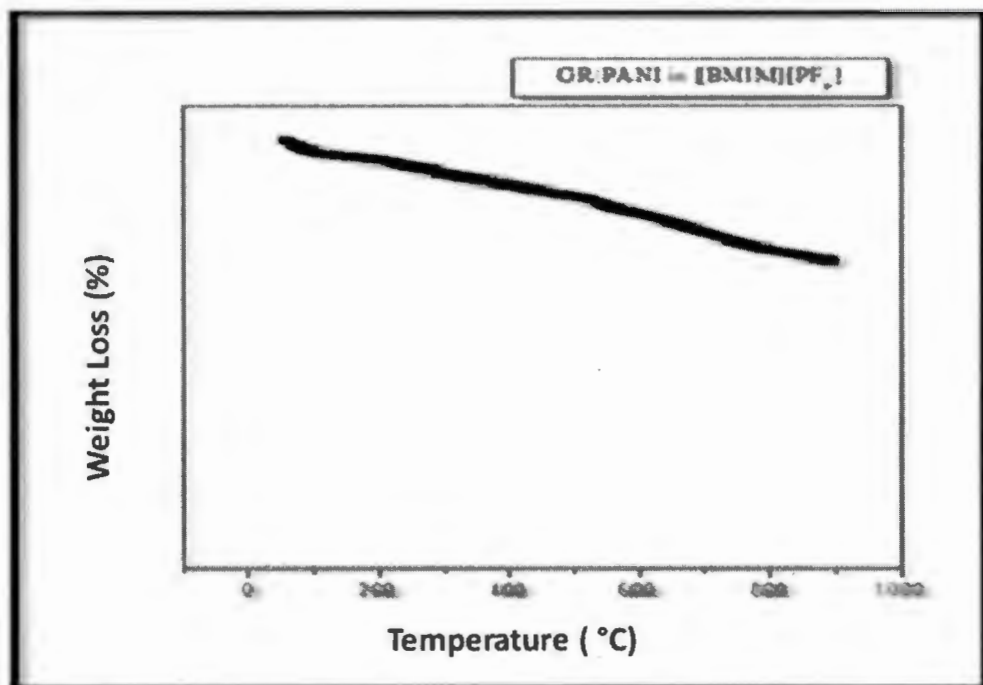


Figure 4.8 d: TGA graph of GR/PANI nanocomposites synthesized in the presence of [BMIM][PF₆]

The GR/PANI nanocomposites (figures 4.8 c-d and 6.32-6.38 (appendix 6.5)) also lost water of intercalation at $\sim 100^{\circ}\text{C}$ and again at around $500\text{--}800^{\circ}\text{C}$ which is attributed to the oxidative degradation of the composite itself^[167,224,226]. There is no further weight loss after 800°C because the residues left after degradation of the composites are inert materials such as carbonized polymer fragments and graphite^[226]. The thermal stability which is shown by steady weight loss suggest that there is a good π - π interaction between graphitic monolayers and polyaniline nanostructures; this is in agreement with the FTIR and UV-Vis results^[224,226].

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1. CONCLUSION

The results showed that graphene wasn't completely reduced and the advantage of this is that the remaining oxygen moieties make it possible to disperse it in different solvents since the completely reduced GR is highly hydrophobic. The synthetic method employed in this study is environmentally friendly, tunable to be used in the synthesis of other reduced graphene oxide-based conducting polymer hybrids (which could be used for diverse technological applications such as in sensors, capacitors and electrodes) and has the advantage of reducing GO and polymerizing polyaniline nanoparticles in a single step.

The SEM micrographs of composites synthesized in ionic liquids showed that the PANI nanofibers were nucleated and agglomerated in between the graphene sheets, while the PANI in composites synthesized in organic liquids formed slippery flakes in between the graphene sheets. The XRD distinctively identified the crystalline structures for GR/PANI nanocomposites synthesized in both ionic liquids and conventional solvents. The crystalline sizes ranged between 89-950 and 29-250 nm for composites synthesized in ionic liquids and organic solvents respectively. The results shown by FTIR, UV-Vis, EDAX and TGA depict that the graphene/polyaniline nanocomposites synthesized in the presence of ionic liquids have similar properties to those synthesized in organic solvents; thus this method could be employed to produce the graphene based conducting polymer nanocomposites as a measure of producing materials in environmentally benign conditions

5.2. RECOMMENDATIONS

The modern world is dependent on sophisticated technological appliances. This technology can only be advanced through thorough research, through imaginative molecular design and synthesis of new materials. The challenges of designing and creating new, reproducible, and

diverse materials are the consumer market, demands to lifestyle improvement, and most importantly the limitations of environment protection and public safety.

The last two issues (environmental protection and public safety) are of vital importance because if researchers continue to use outdated methods there may be rapid rates of global warming which may result in extinction of some species especially the ones which are regarded as “Rare species”, and the growth of diseases. It is important to try to produce new technology using methods which are environmentally friendly. This could be achieved by development of synthetic methods and design of safer chemicals. In this study safer chemicals such as ionic liquids were used.

The results after synthesizing the composites in these green solvents showed that this method could be used to prepare graphene/polyaniline nanohybrids which have properties which correspond to those of composites synthesized in organic solvents and aqueous solutions.

It is recommended that ionic liquids (green solvents) should be used as substitutes for previously used reaction media and that conductivity and rheology studies of these composites should be carried out and also synthesize these hybrids in other ionic solvents.

CHAPTER 6

APPENDICES

APPENDIX 6.1: ENERGY DISPERSIVE X-RAY ANALYSIS (EDAX)

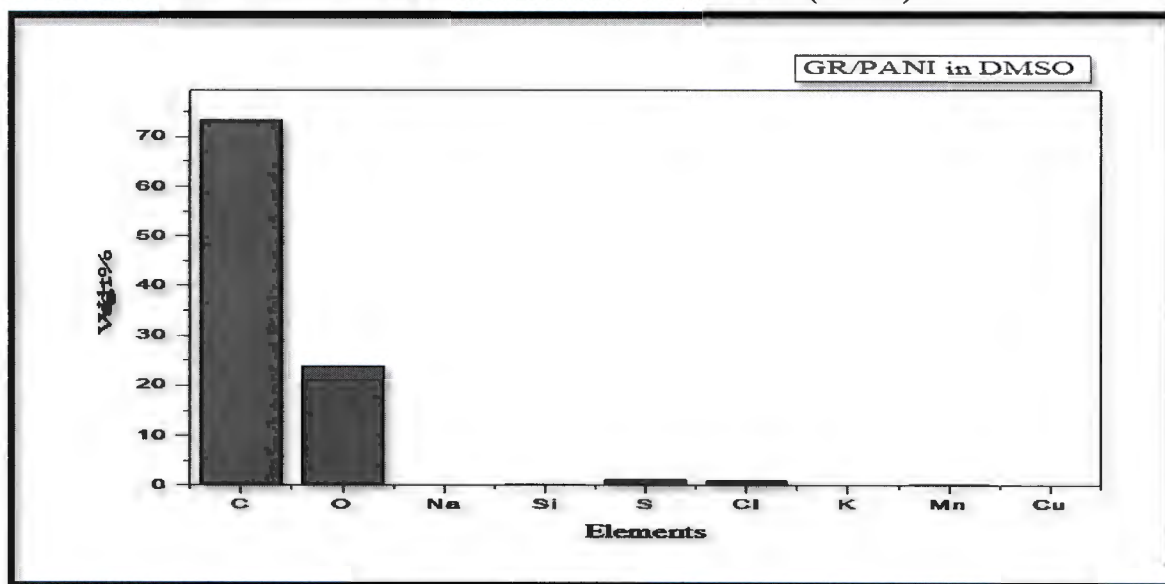


Figure 6.1: EDAX of GR/PANI synthesized in DMSO.

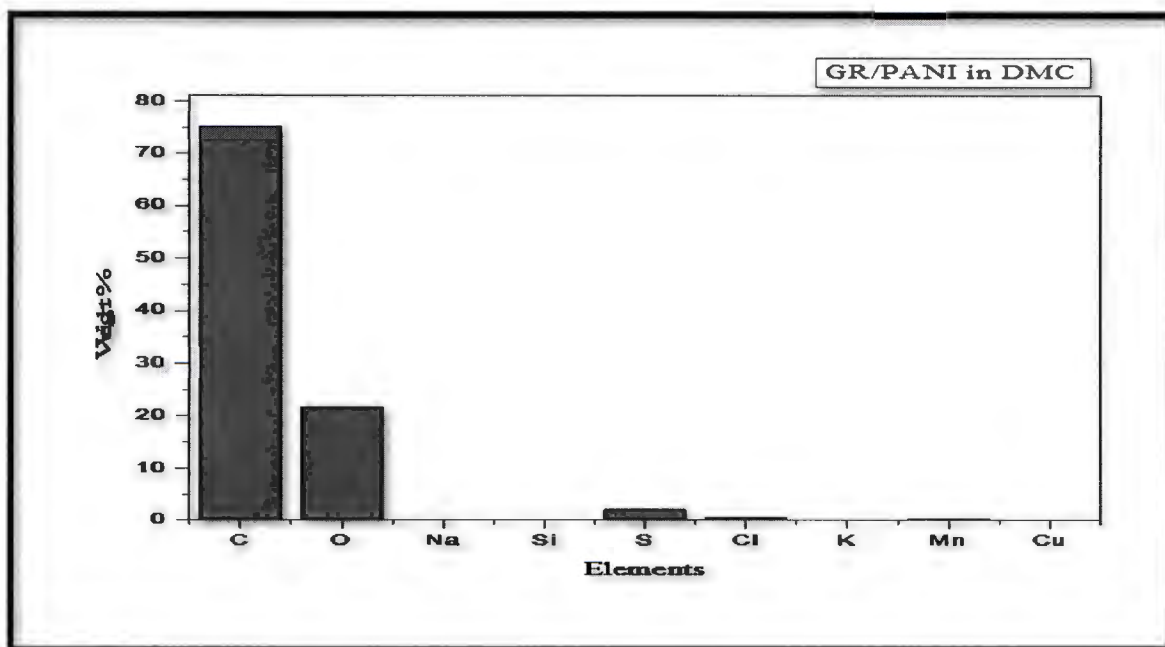


Figure 6.2: EDAX of GR/PANI synthesized in DMC.

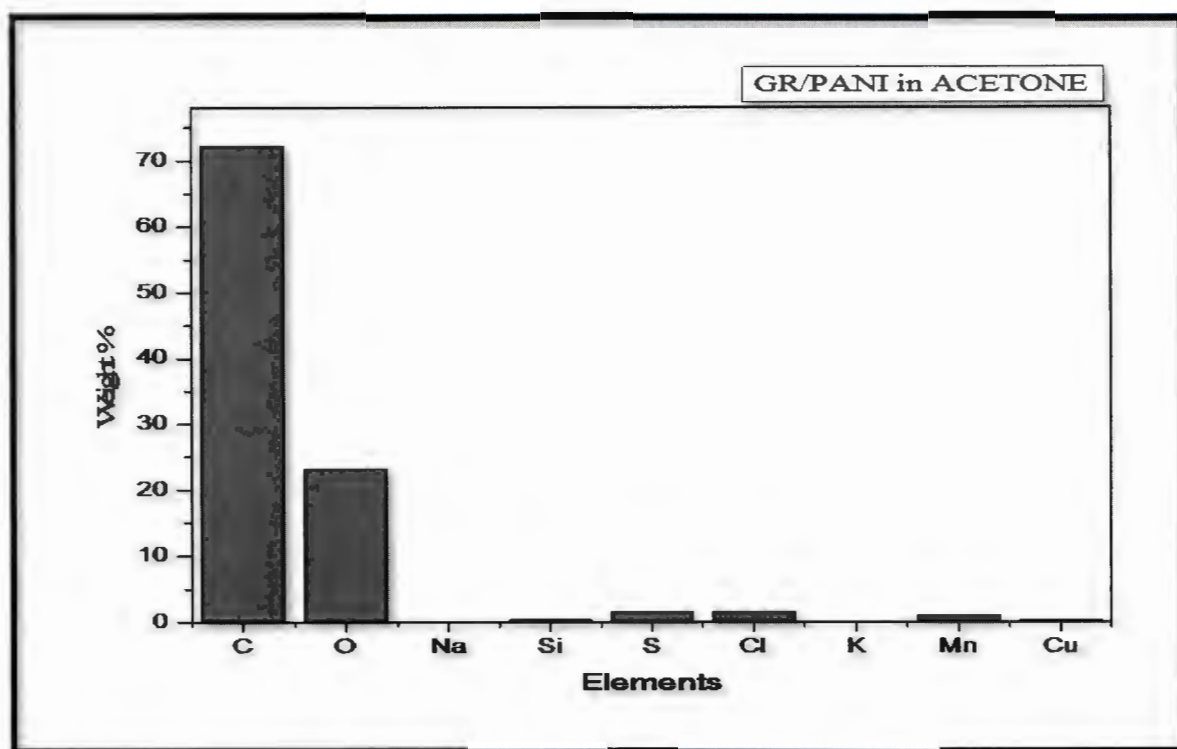


Figure 6.3: EDAX of GR/PANI synthesized in acetone.

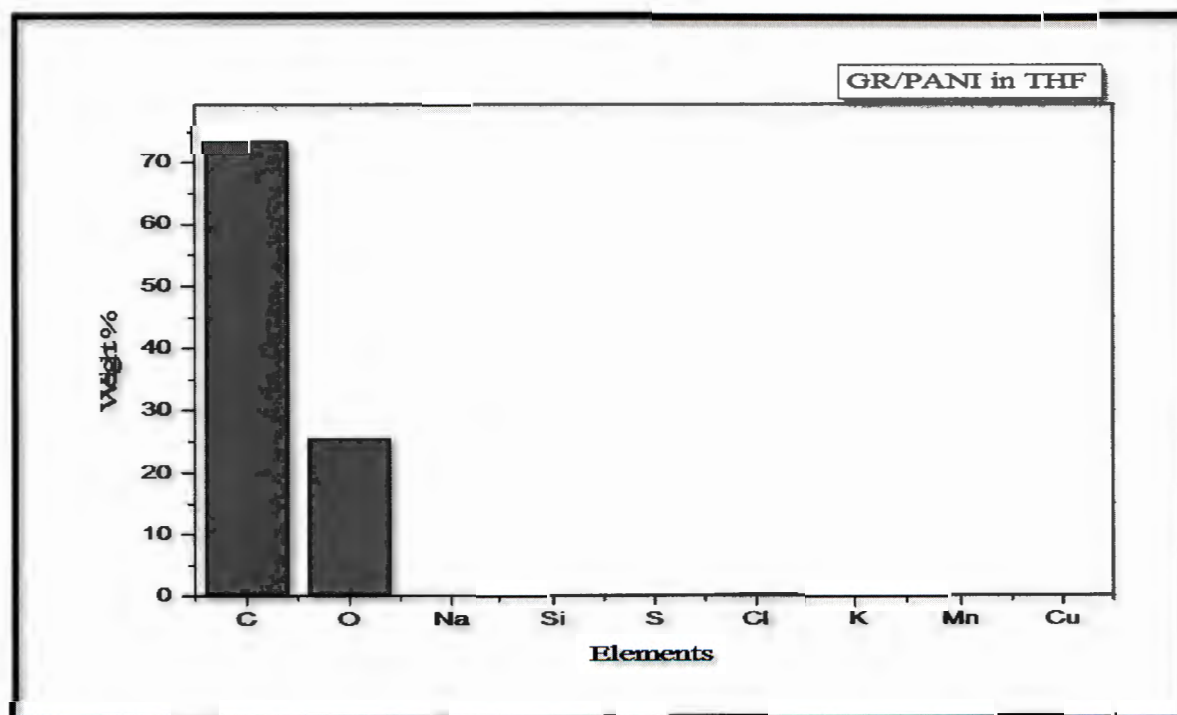


Figure 6.4: EDAX of GR/PANI synthesized in THF.

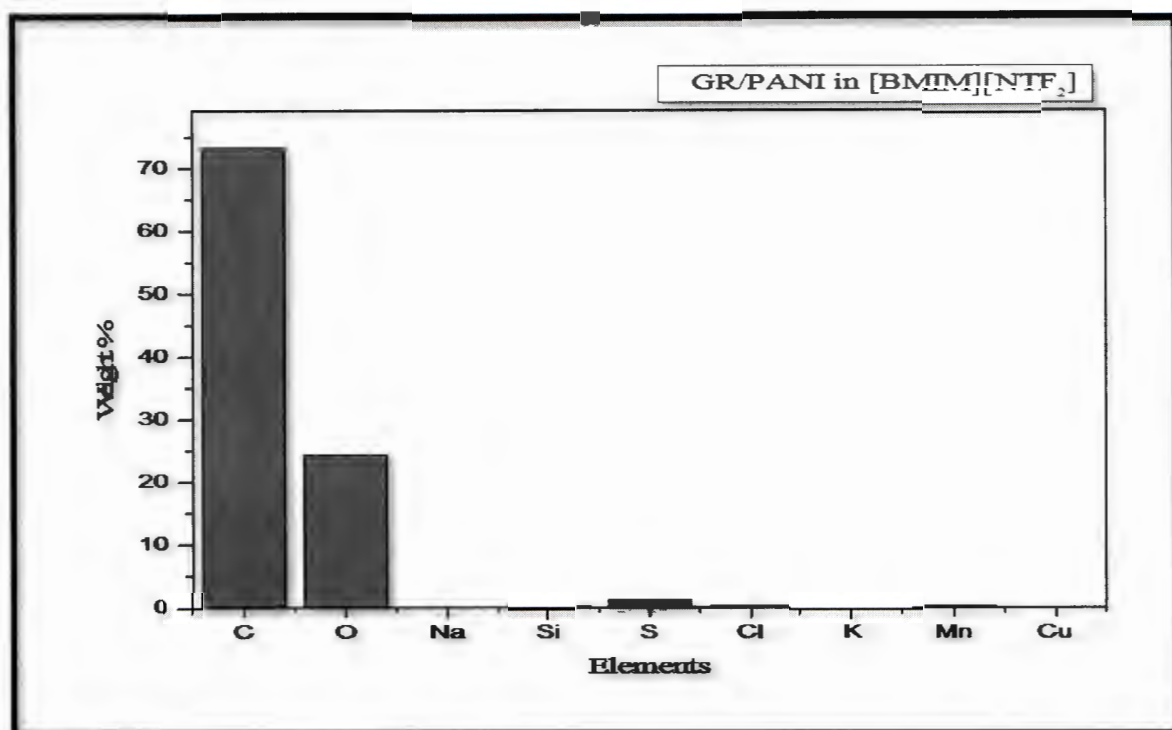


Figure 6.5: EDAX of GR/PANI synthesized in [BMIM][NTF₂].

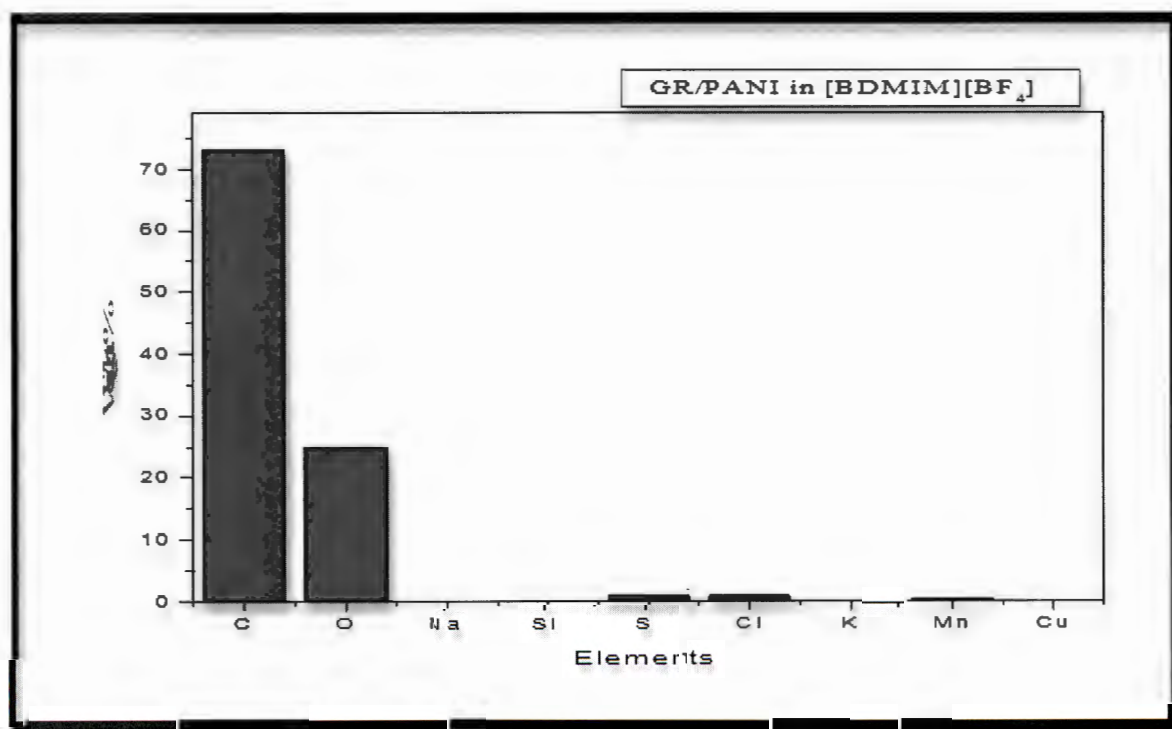


Figure 6.6: EDAX of GR/PANI synthesized in [BDMIM][BF₄].

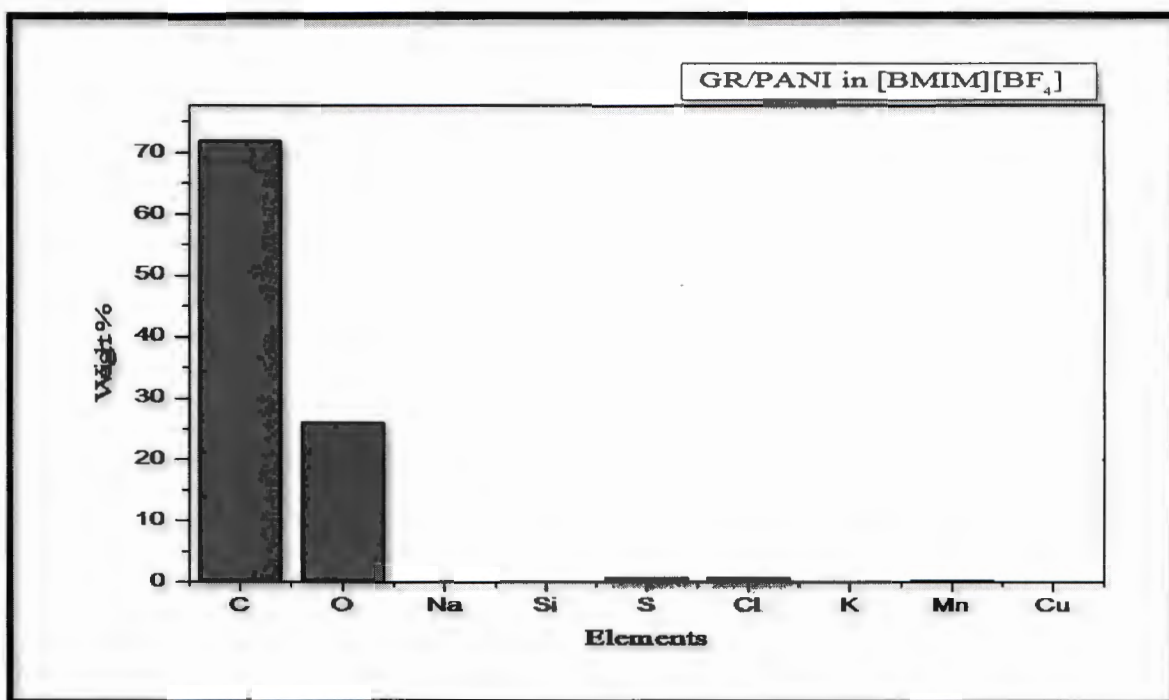


Figure 6.7: EDAX of GR/PANI synthesized in [BMIM][BF₄].

APPENDIX 6.2: X-RAY DIFFRACTOMETOR (XRD)

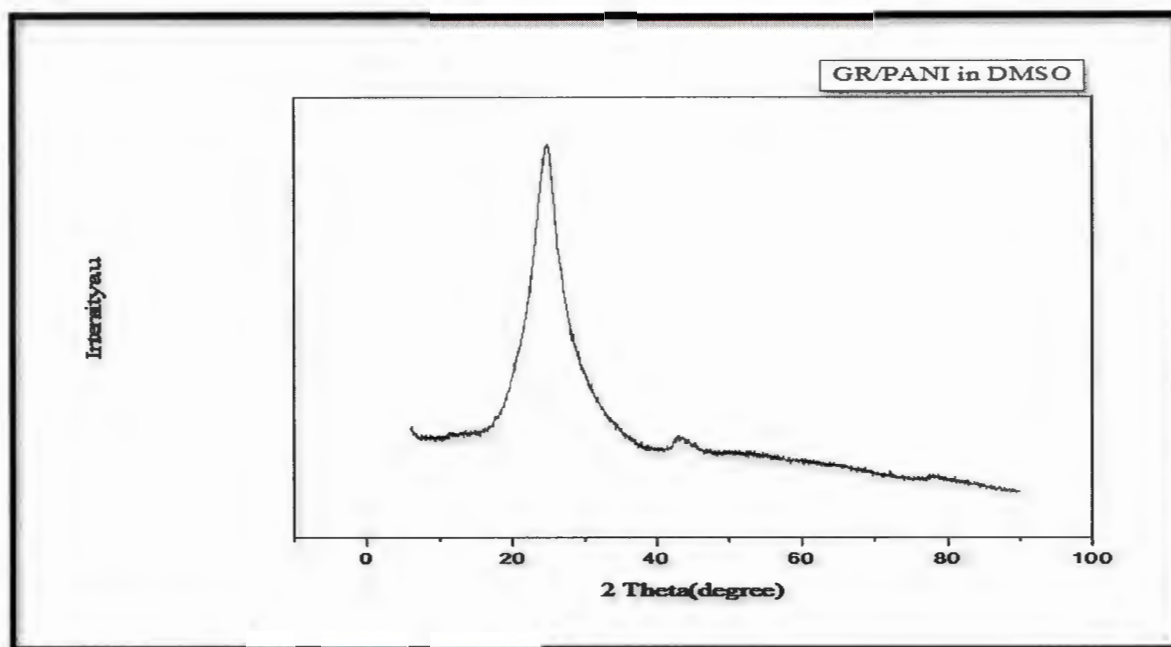


Figure 6.8: XRD of GR/PANI nanocomposites synthesized in DMSO.

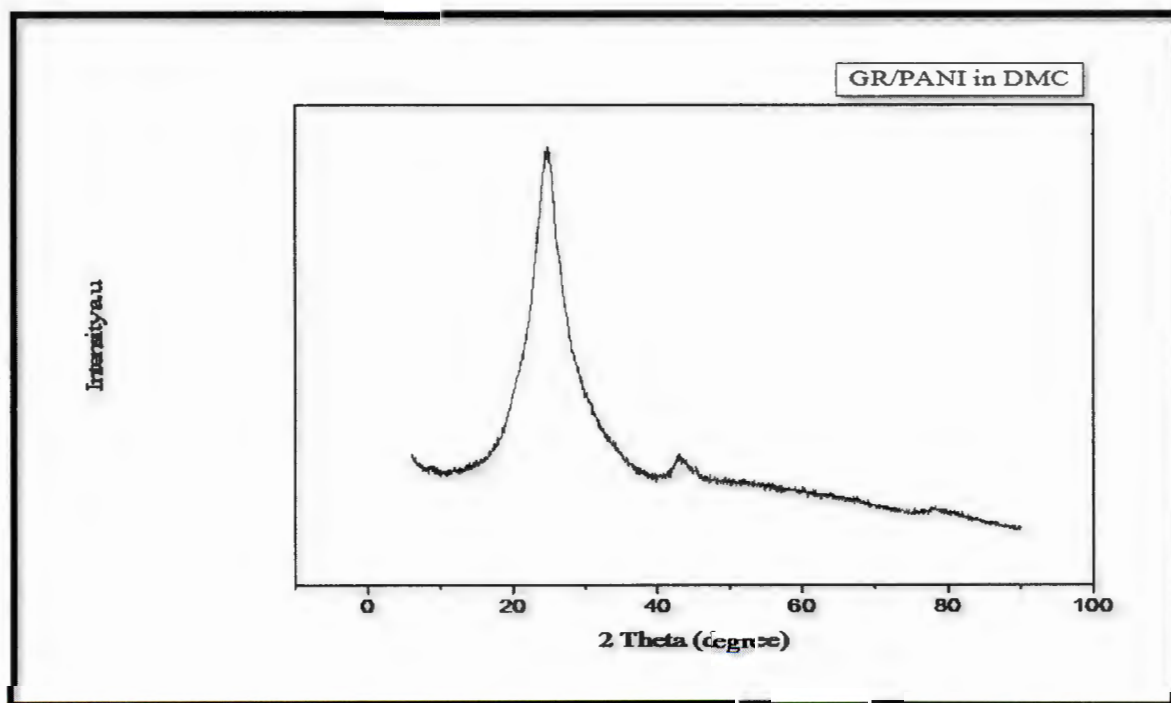


Figure 6.9: XRD of GR/PANI nanocomposites synthesized in DMC.

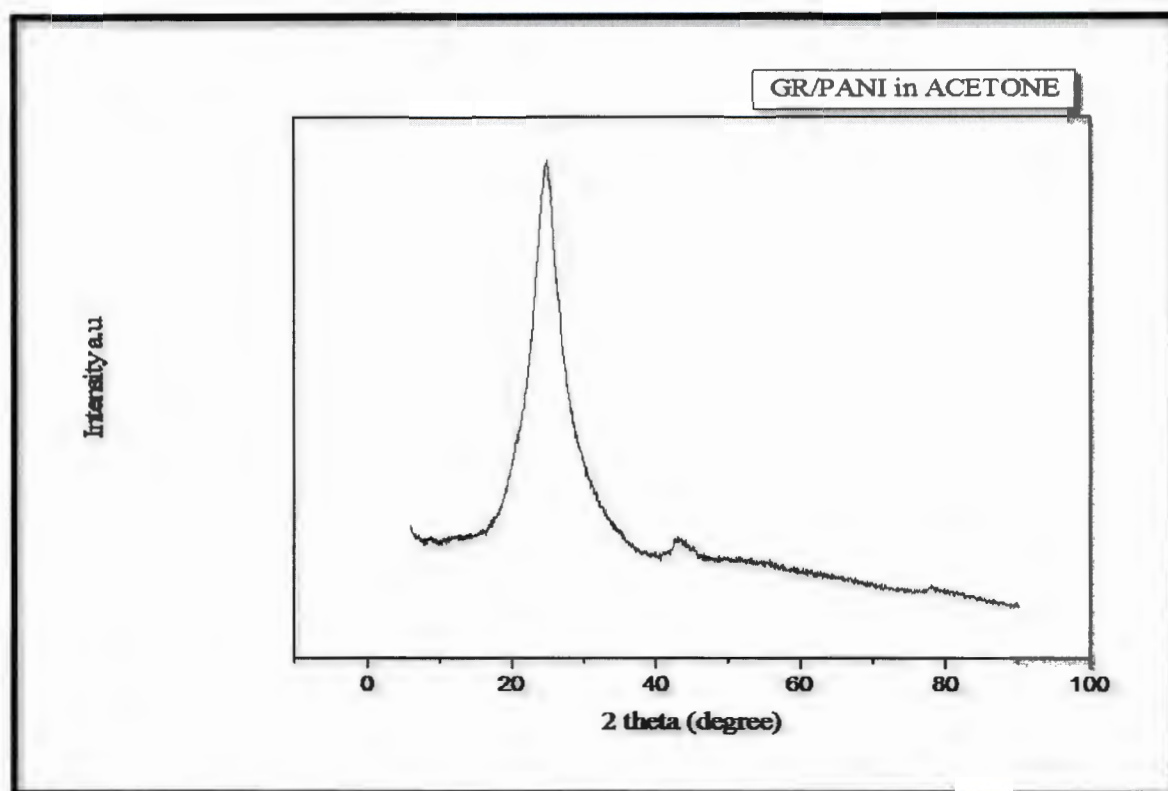


Figure 6.10: XRD of GR/PANI nanocomposites synthesized in acetone.

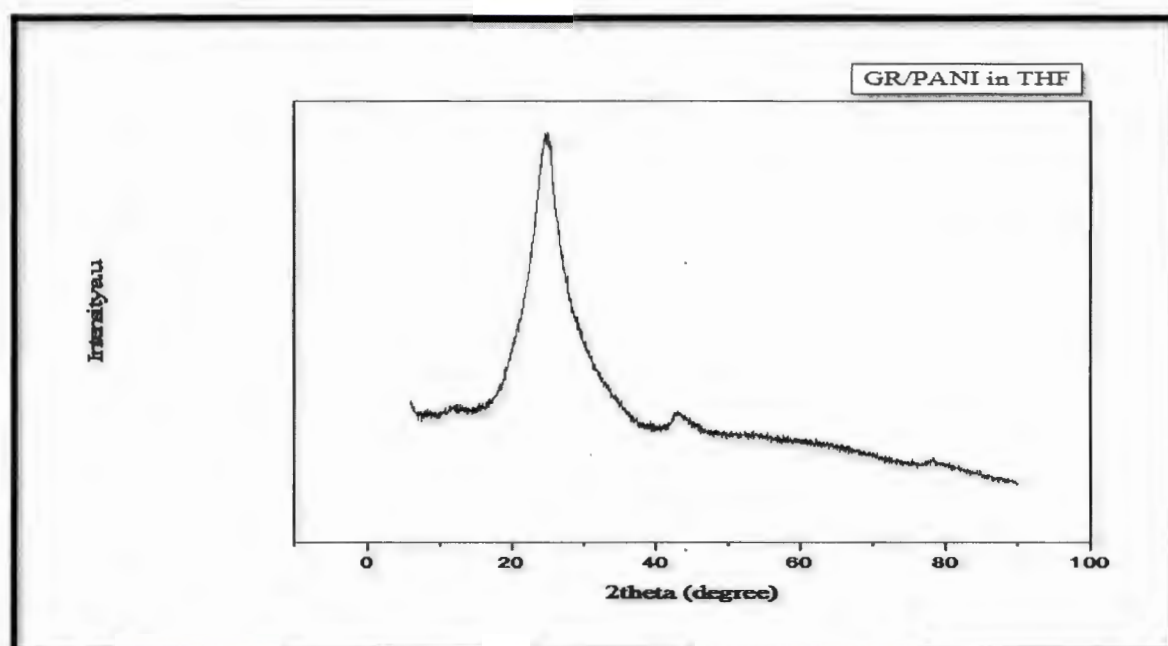


Figure 6.11: XRD of GR/PANI nanocomposites synthesized in THF.

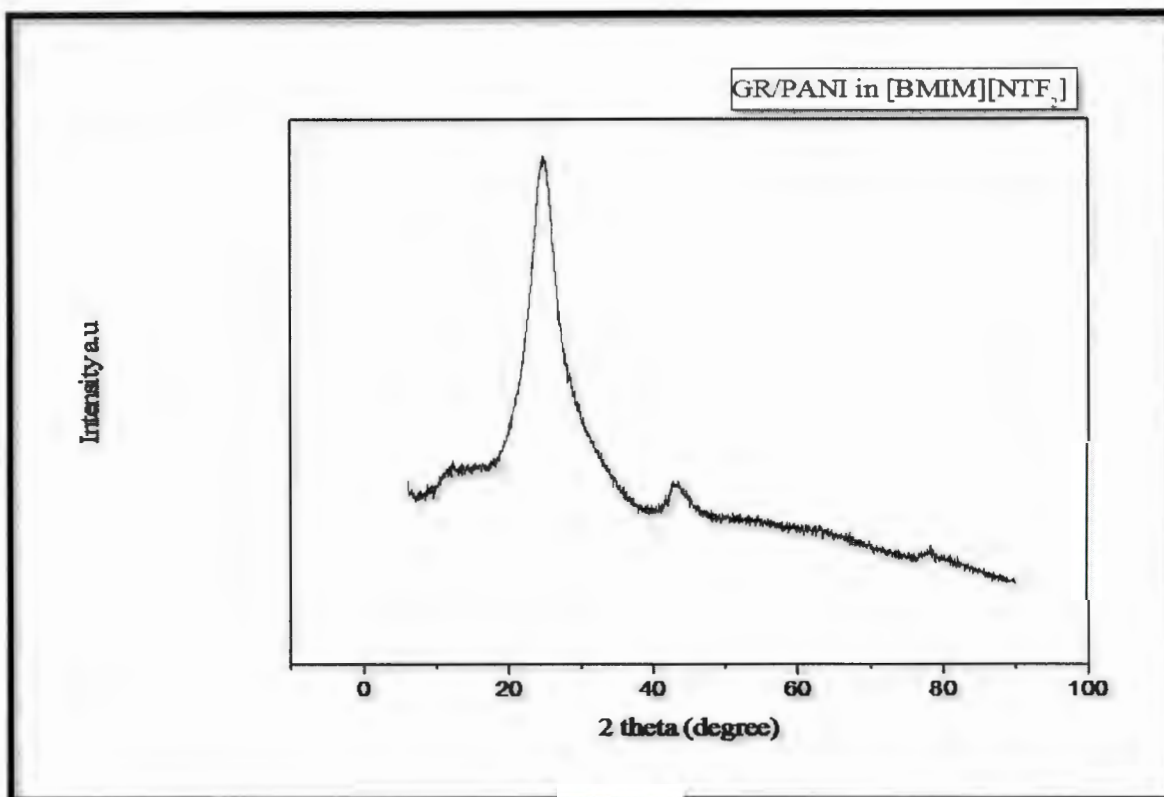


Figure 6.12: XRD of GR/PANI nanocomposites synthesized in [BMIM][NTF₂].

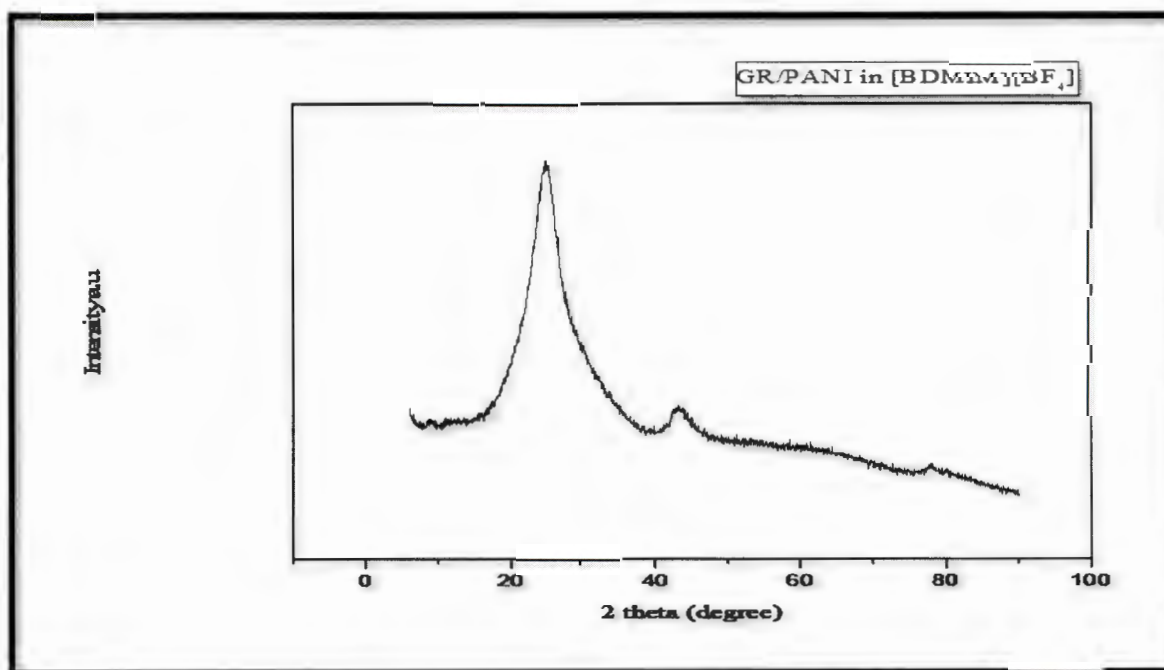


Figure 6.13: XRD of GR/PANI nanocomposites synthesized in [BDMIM][BF₄].

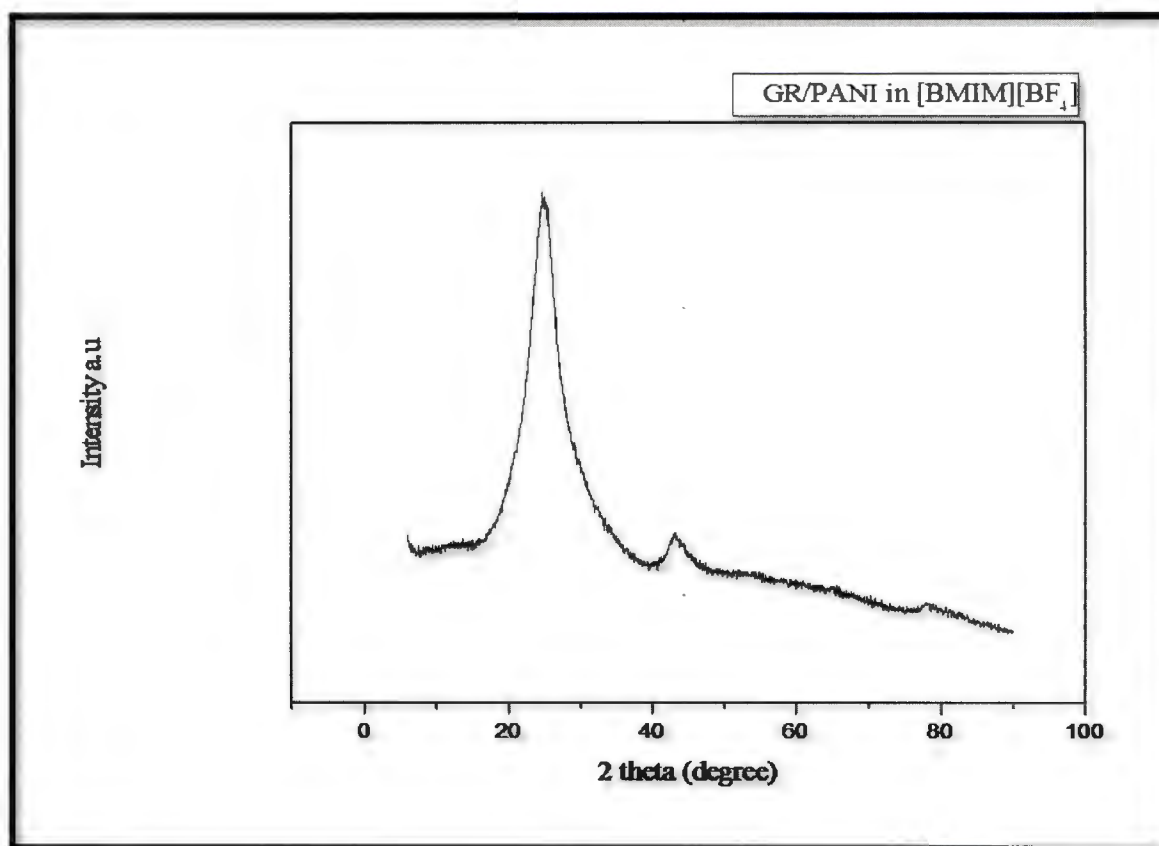


Figure 6.14: XRD of GR/PANI nanocomposites synthesized in [BMIM][BF₄].

APPENDIX 6.3: FOURIER TRANSFORM INFRARED SPECTROSCOPY

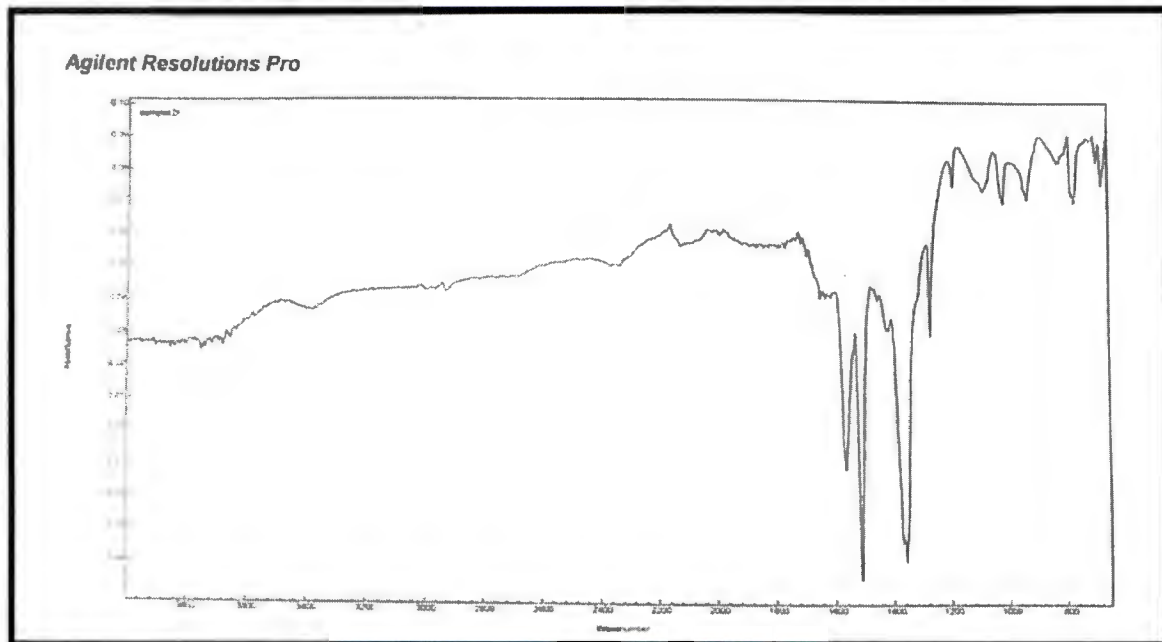


Figure 6.15: The FTIR spectrum of GO

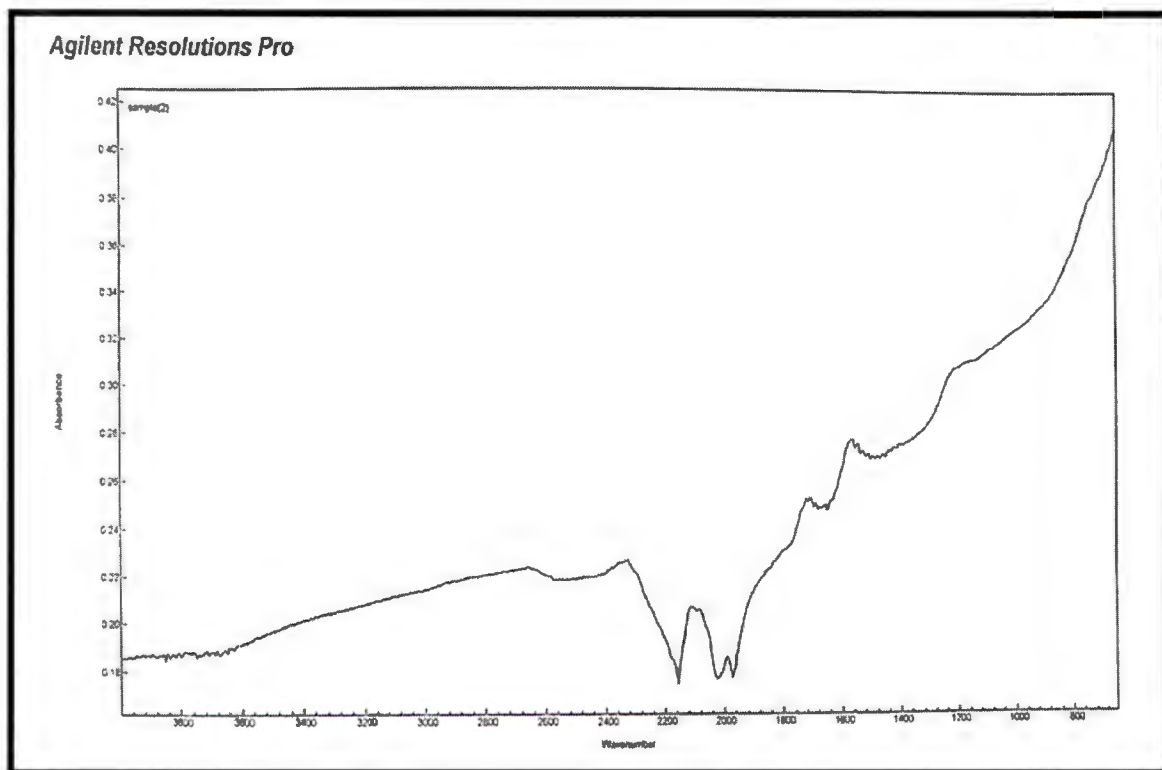


Figure 6.16: The FTIR spectrum of GR

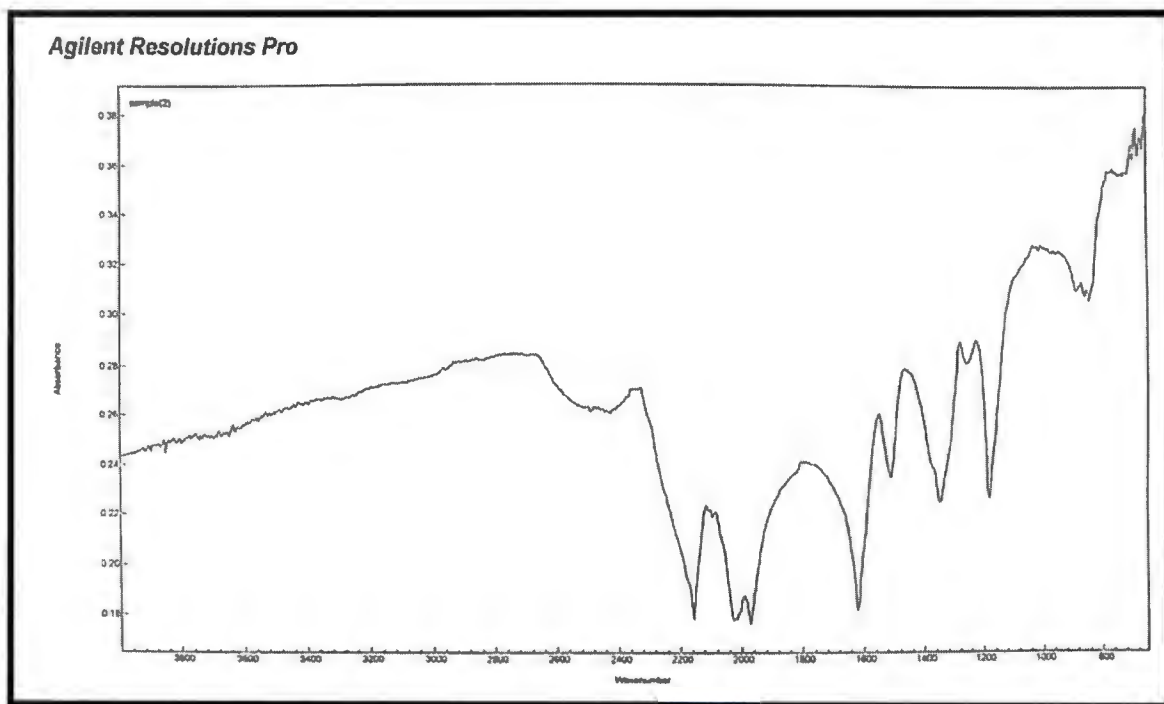


Figure 6.17: The FTIR spectrum of PANI

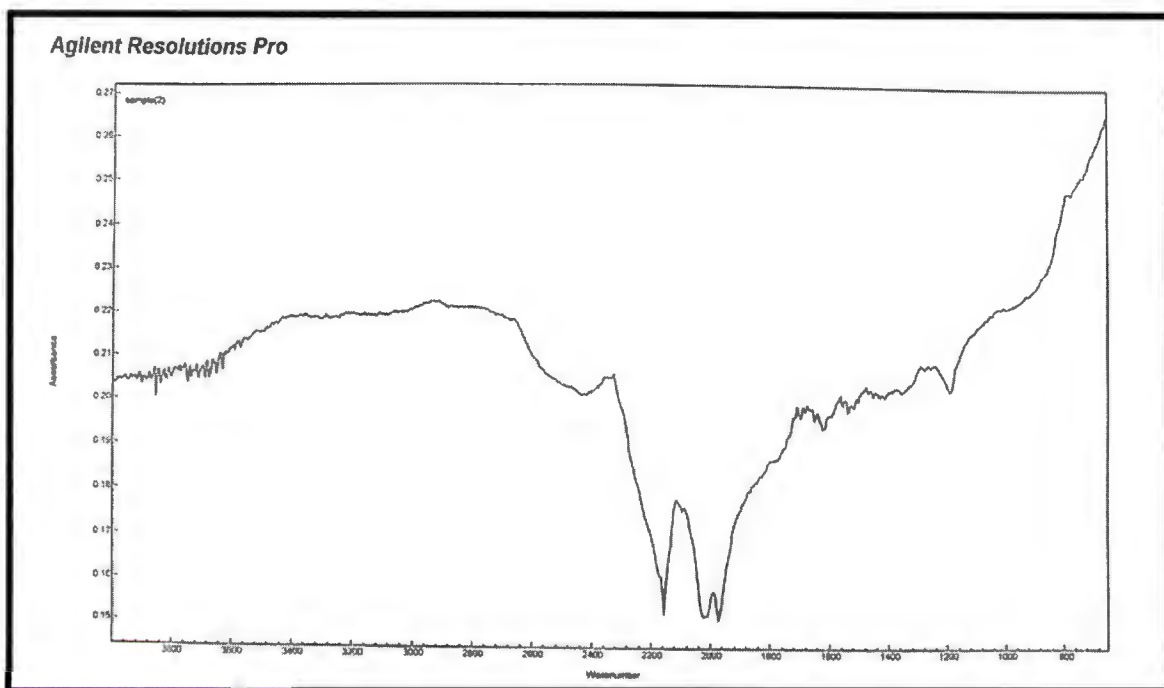


Figure 6.18: The FTIR spectrum of GR/PANI nanocomposites synthesized in toluene

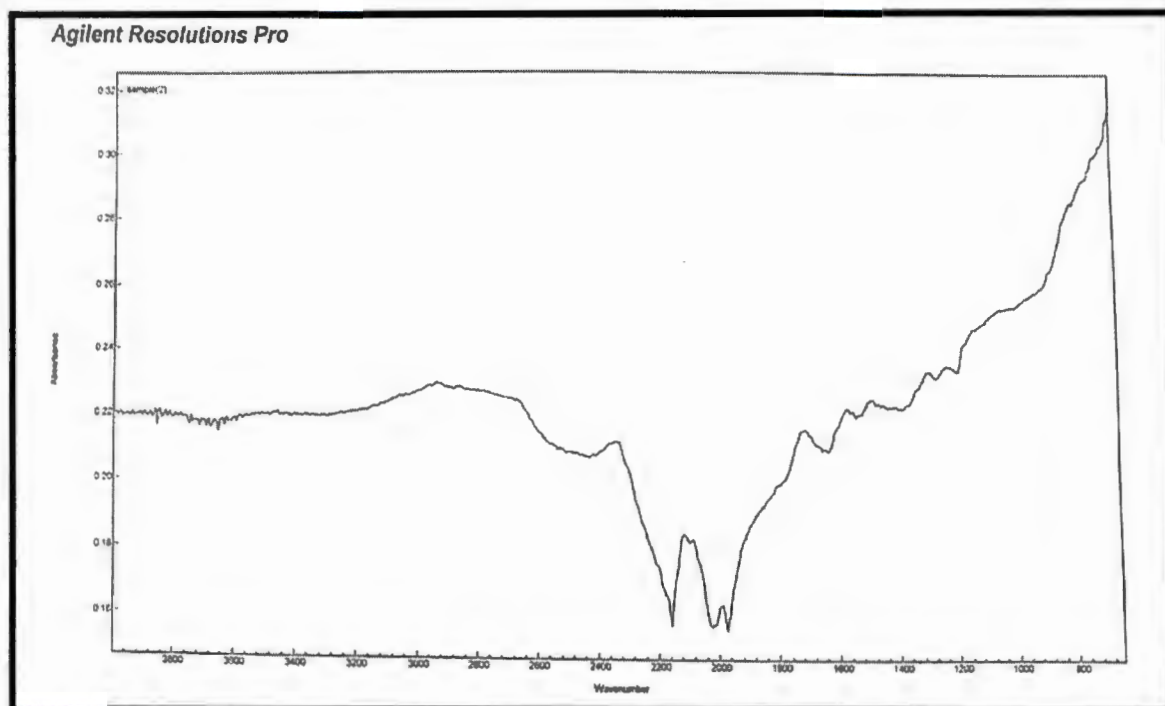


Figure 6.19: The FTIR spectrum of GR/PANI nanocomposites synthesized in DMSO

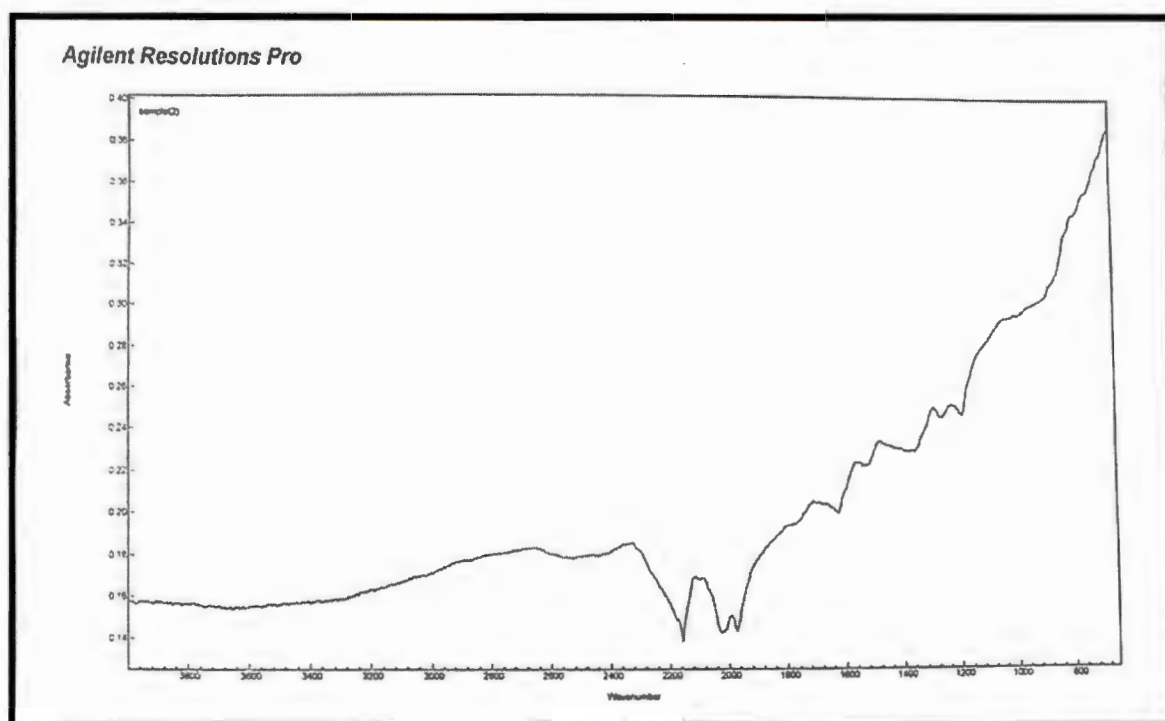


Figure 6.20: The FTIR spectrum of GR/PANI nanocomposites synthesized in DMC

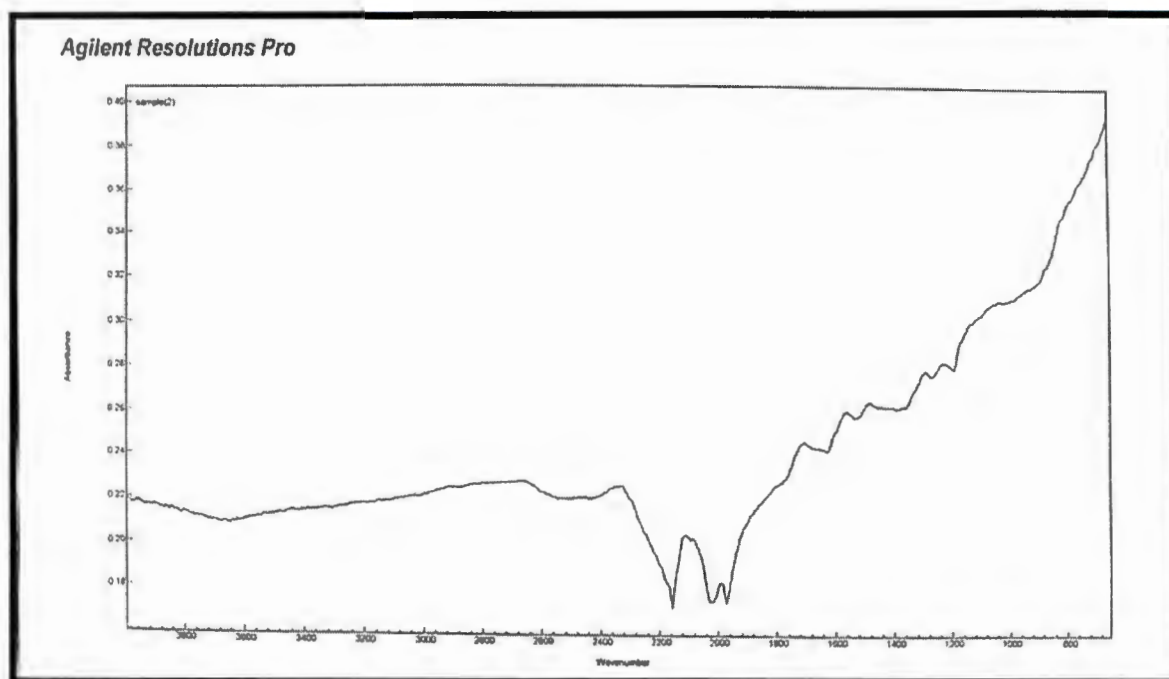


Figure 6.21: The FTIR spectrum of GR/PANI nanocomposites synthesized in acetone

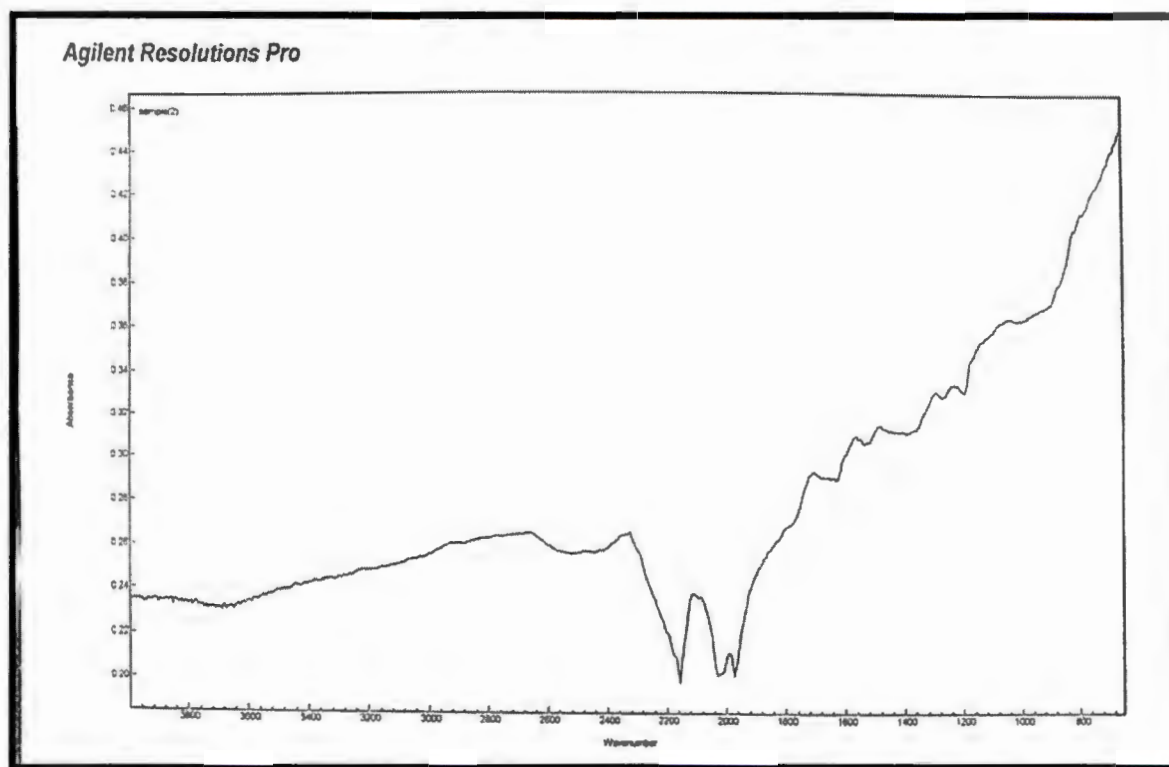


Figure 6.21: The FTIR spectrum of GR/PANI nanocomposites synthesized in THF

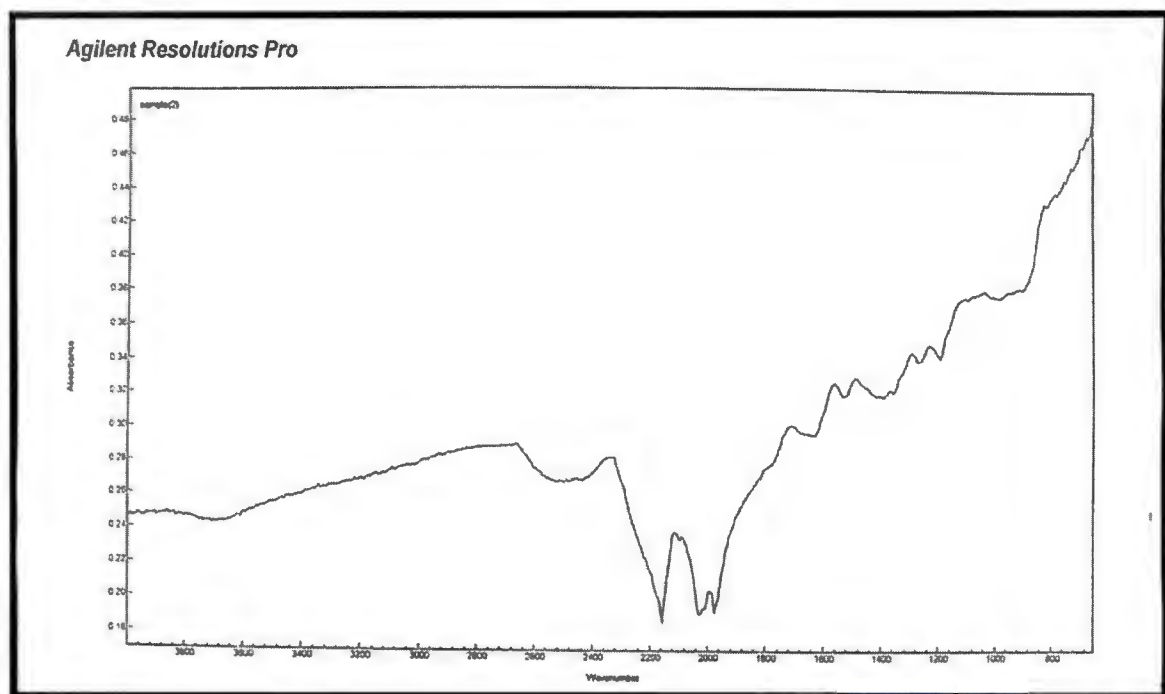


Figure 6.22: The FTIR spectrum of GR/PANI nanocomposites synthesized in [BMIM][PF₆]

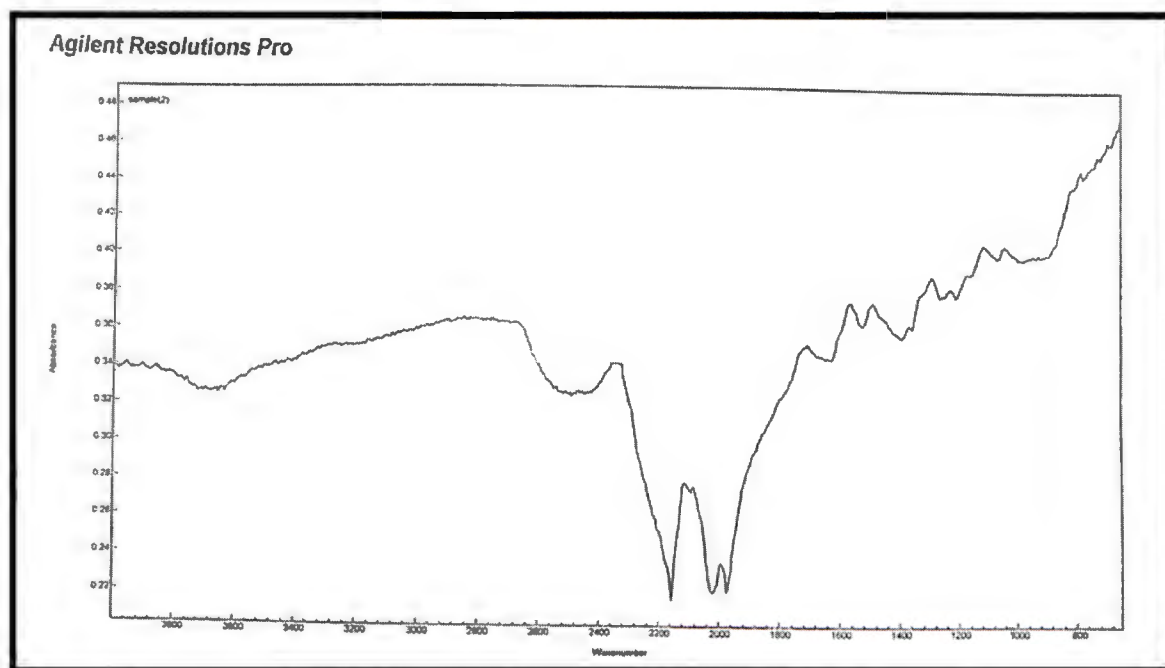


Figure 6.23: The FTIR spectrum of GR/PANI nanocomposites synthesized in [BMIM][NTF₂]

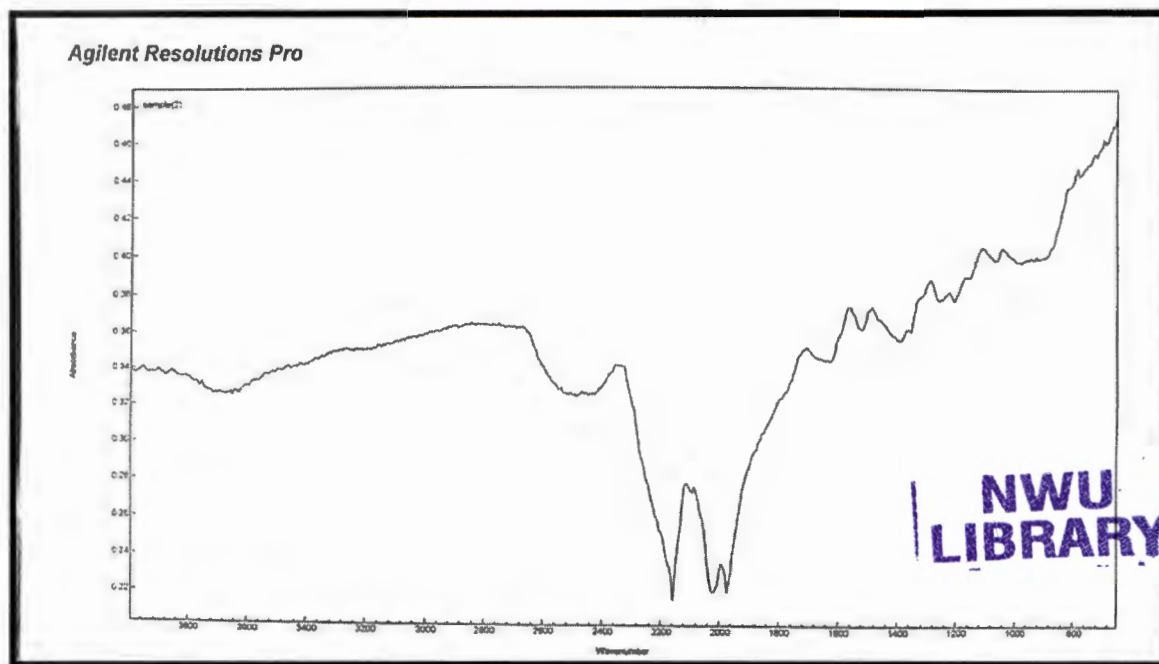


Figure 6.24: The FTIR spectrum of GR/PANI nanocomposites synthesized in [BDMIM][BF₄]

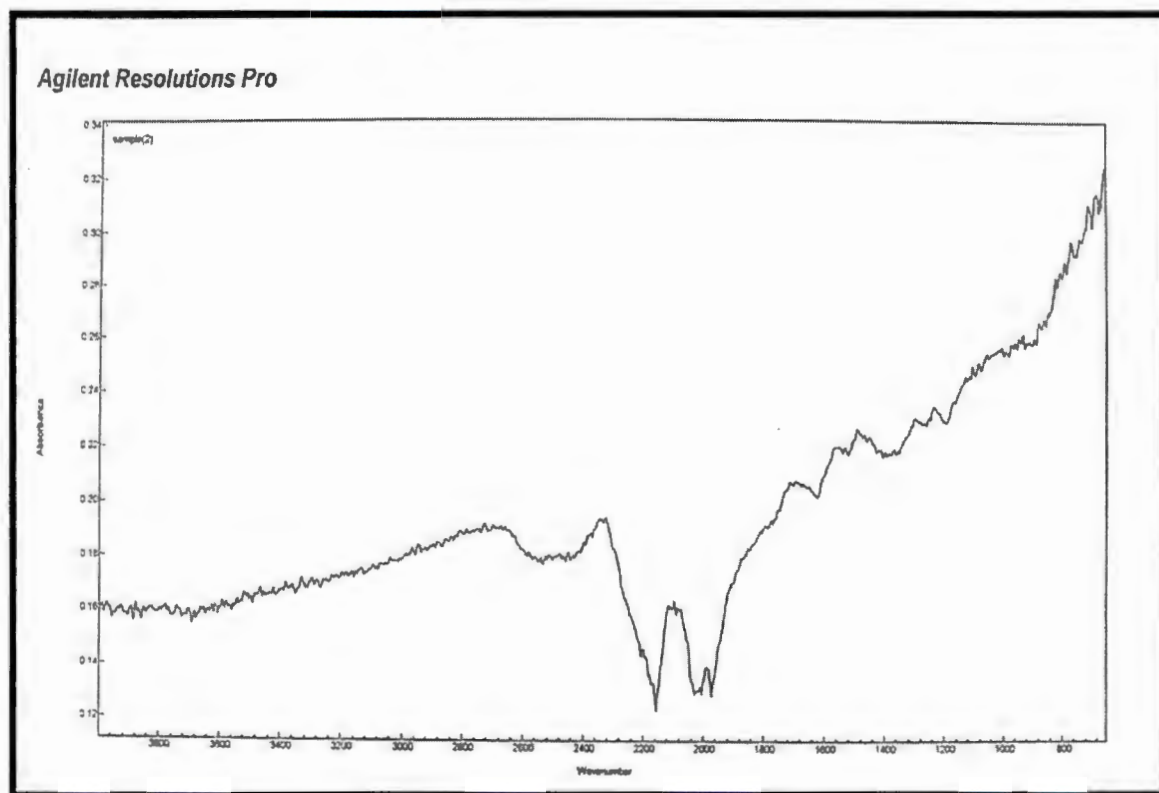


Figure 6.25: The FTIR spectrum of GR/PANI nanocomposites synthesized in [BMIM][BF₄]

APPENDIX 6.4: ULTRA VIOLET VISIBLE SPECTROSCOPY

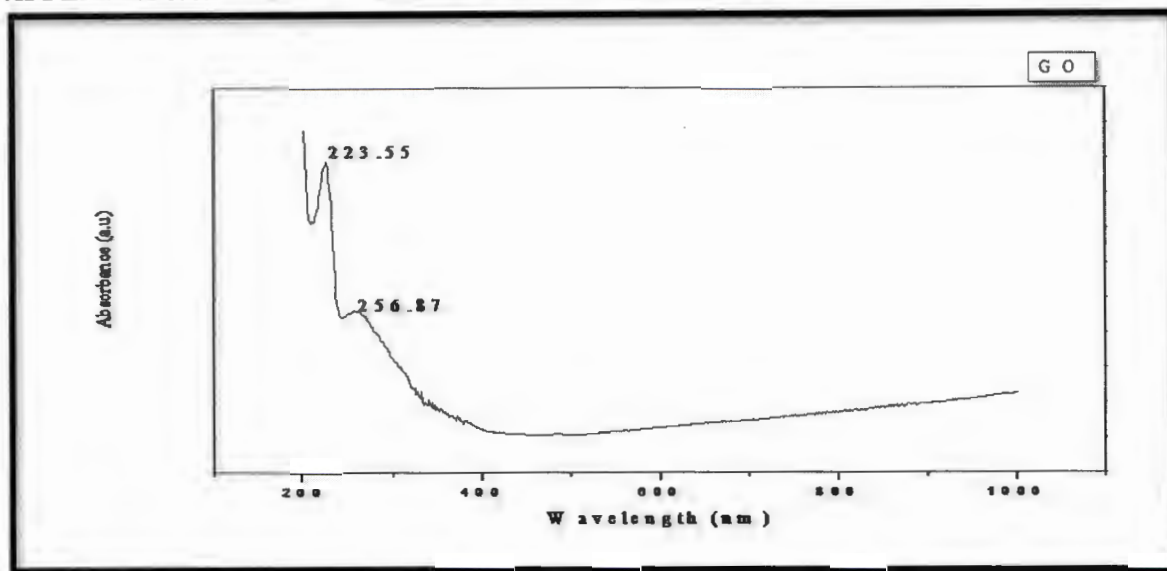


Figure 6.27: UV-Vis spectrum of graphene oxide (GO)

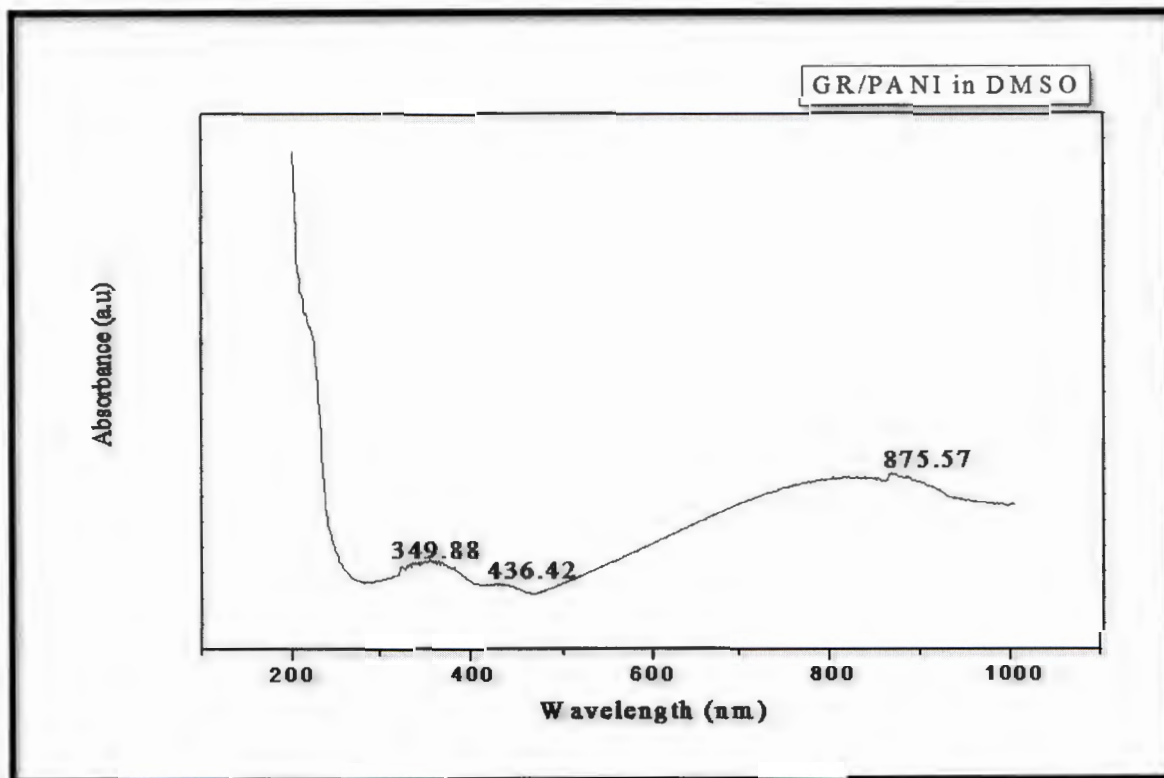


Figure 6.28: UV-Vis spectrum of GR/PANI nanocomposites in DMSO

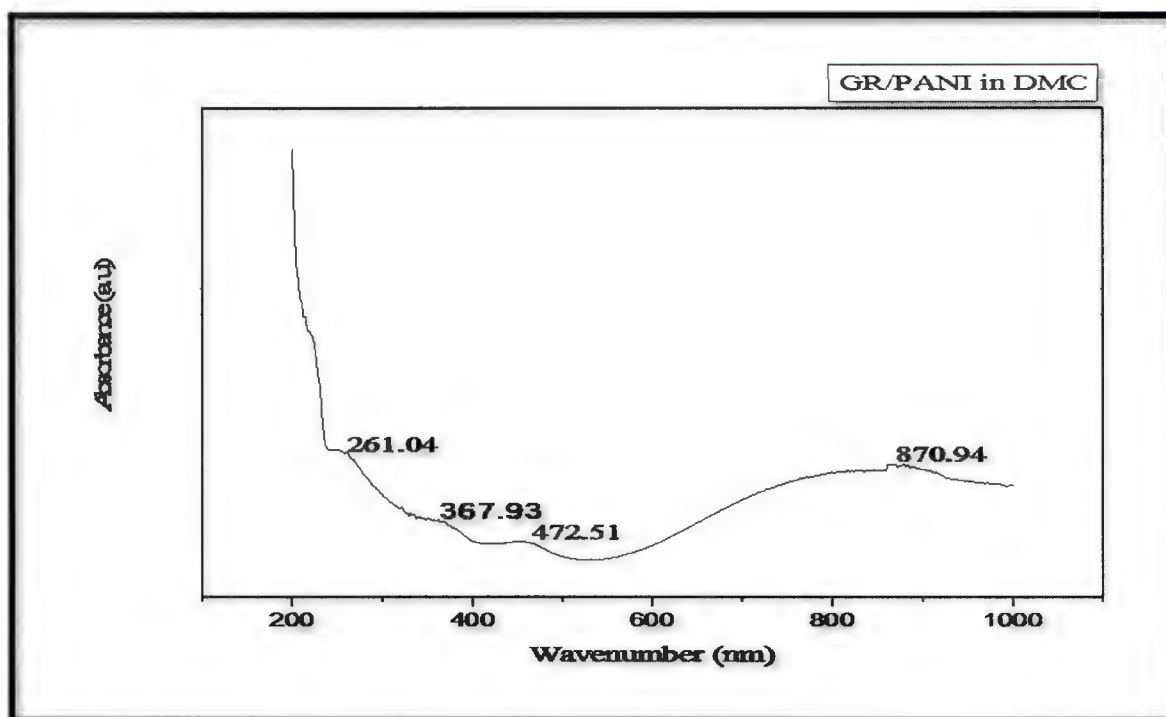


Figure 6.29: UV-Vis spectrum of GR/PANI nanocomposites in DMC

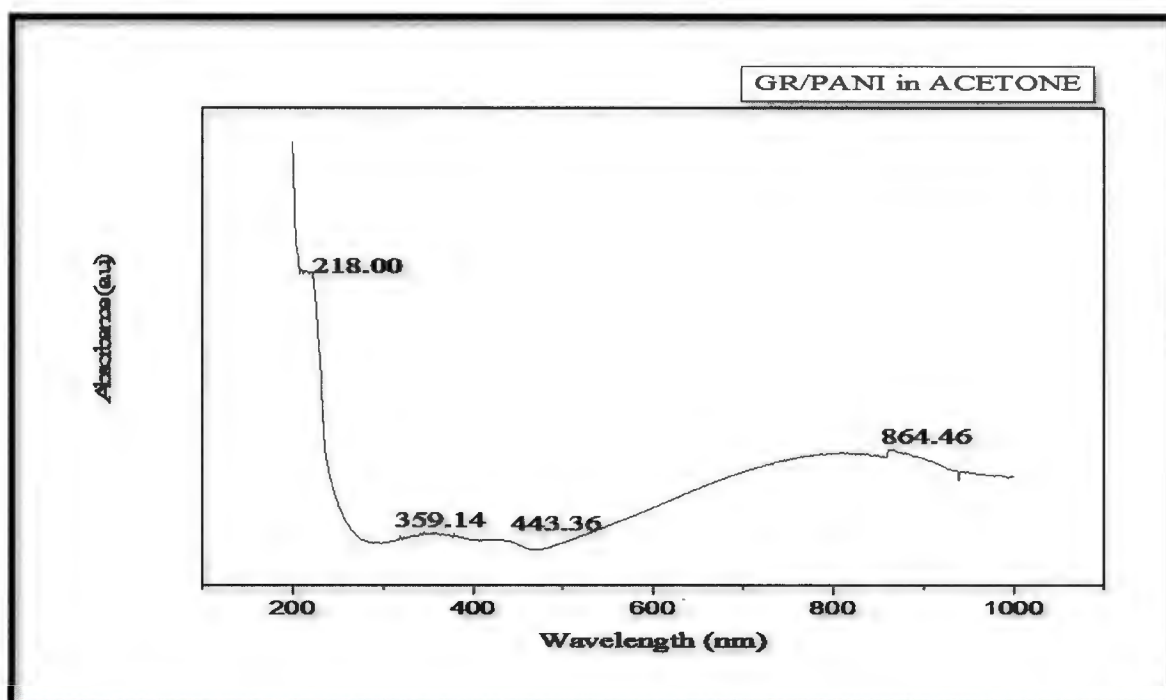


Figure 6.30: UV-Vis spectrum of GR/PANI nanocomposites in ACETONE

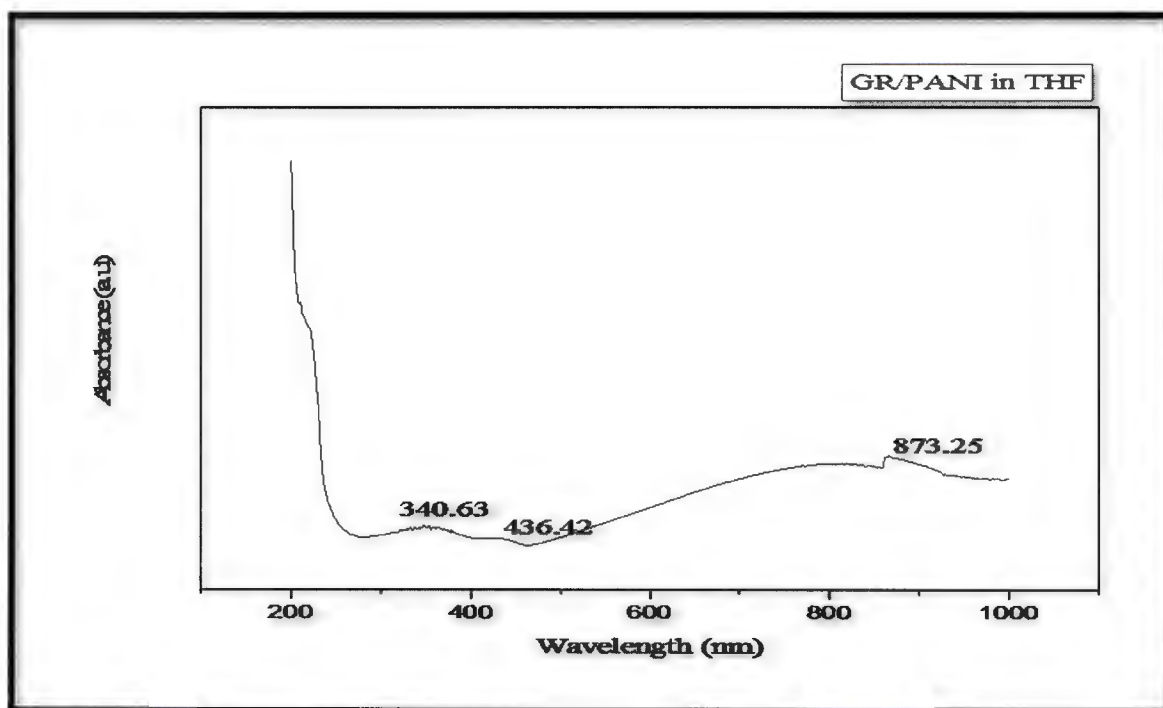


Figure 6.31: UV-Vis spectrum of GR/PANI nanocomposites in THF

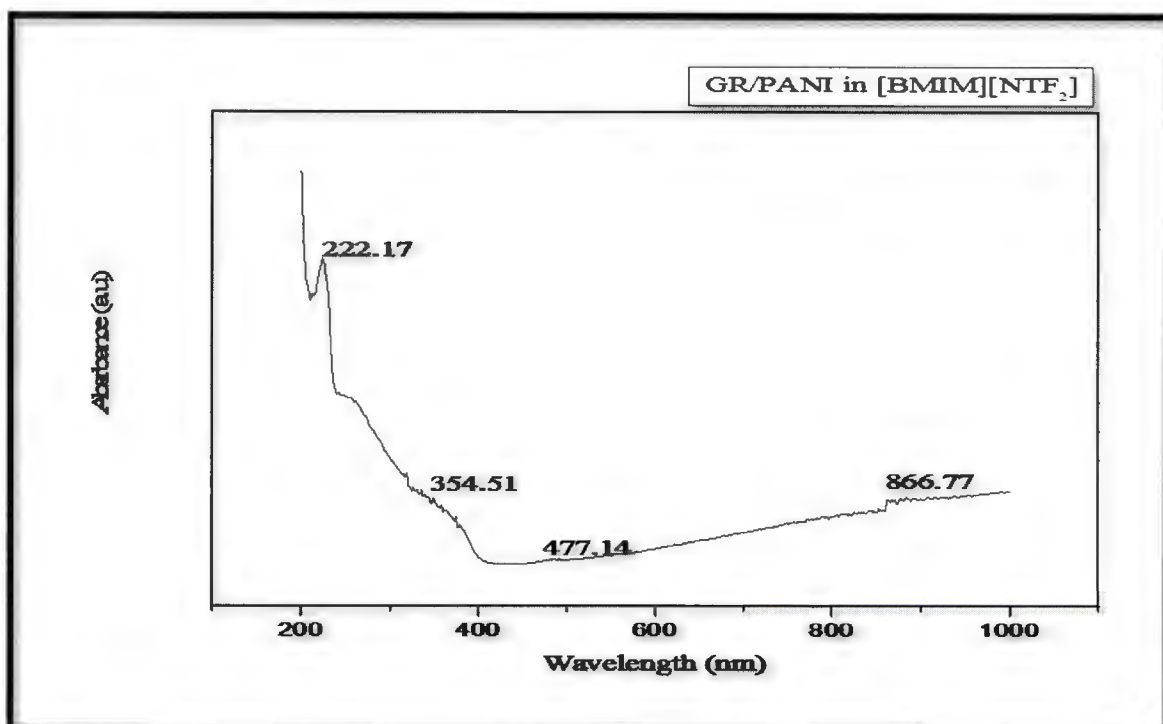


Figure 6.32: UV-Vis spectrum of GR/PANI nanocomposites in [BMIM][NTF₂]

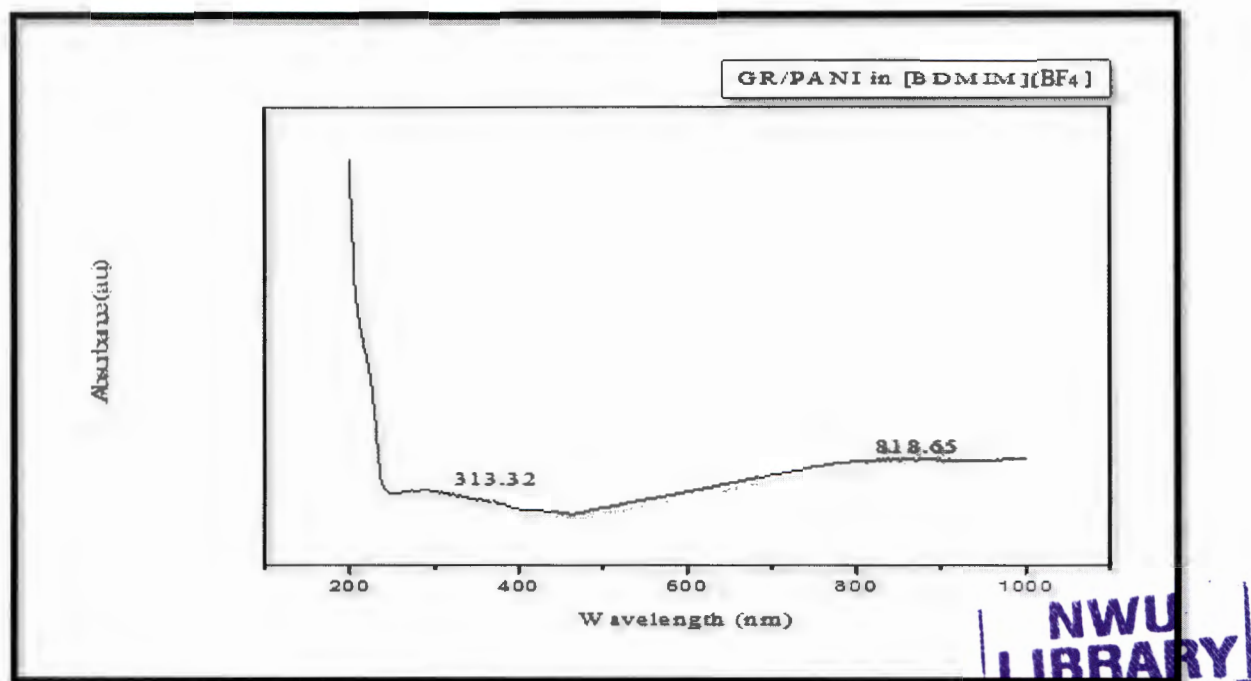


Figure 6.33: UV-Vis spectrum of GR/PANI nanocomposites in [BDMIM][BF₄]

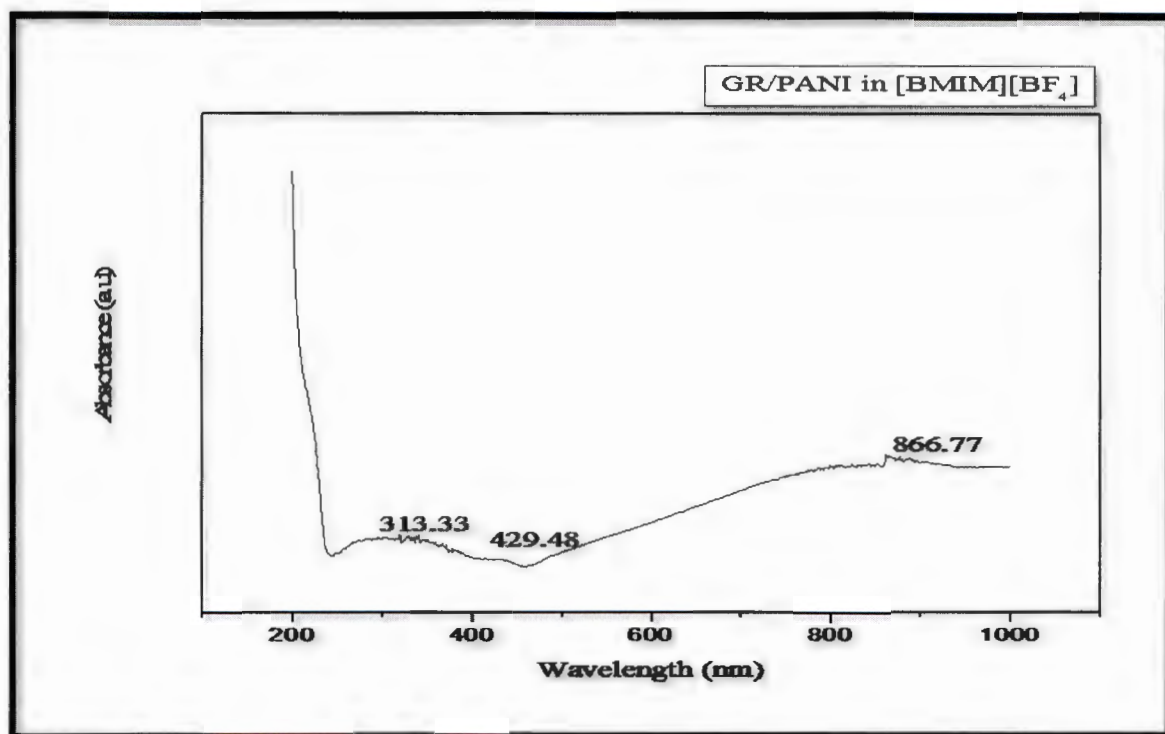


Figure 6.34: UV-Vis spectrum of GR/PANI nanocomposites in [BMIM][BF₄]

APPENDIX 6.5: THERMOGRAVIMMETRIC ANALYSIS

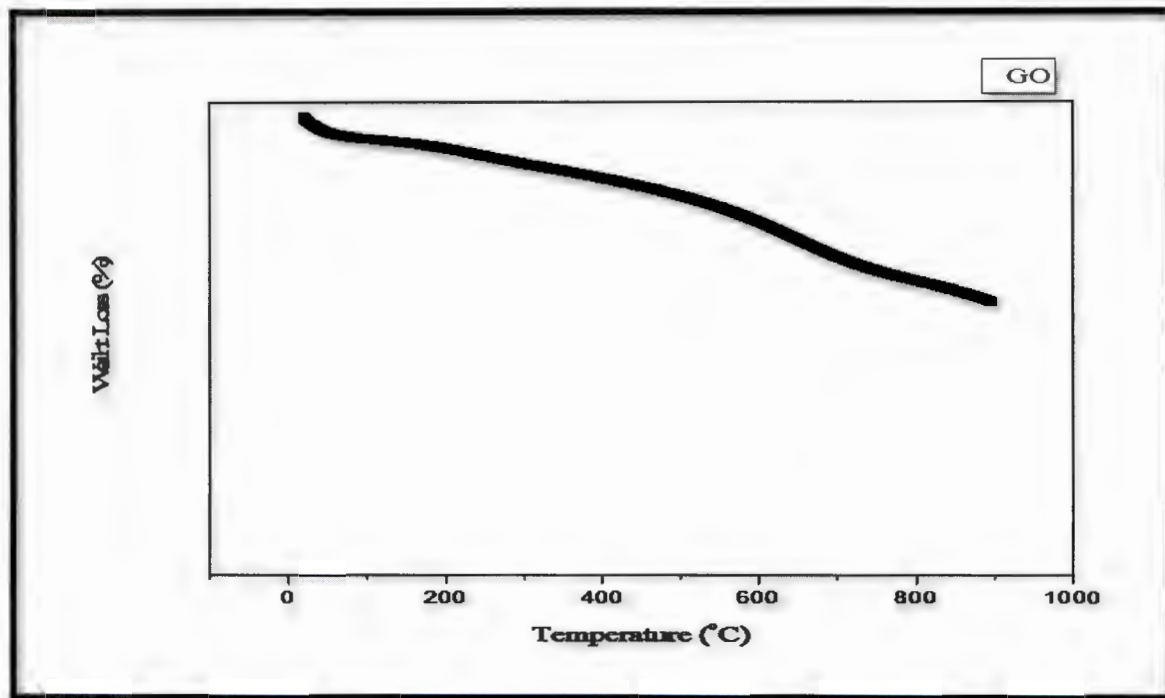


Figure 6.35: TGA graph of GO

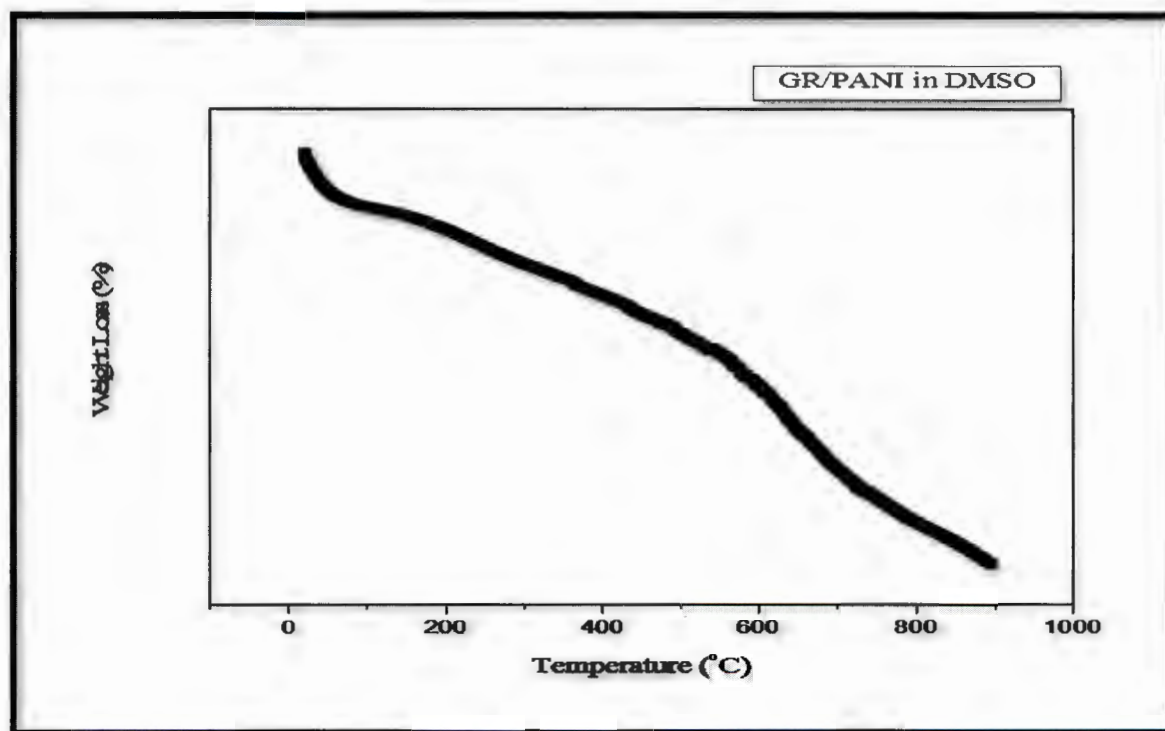


Figure 6.36: TGA graph of GR/PANI in DMSO

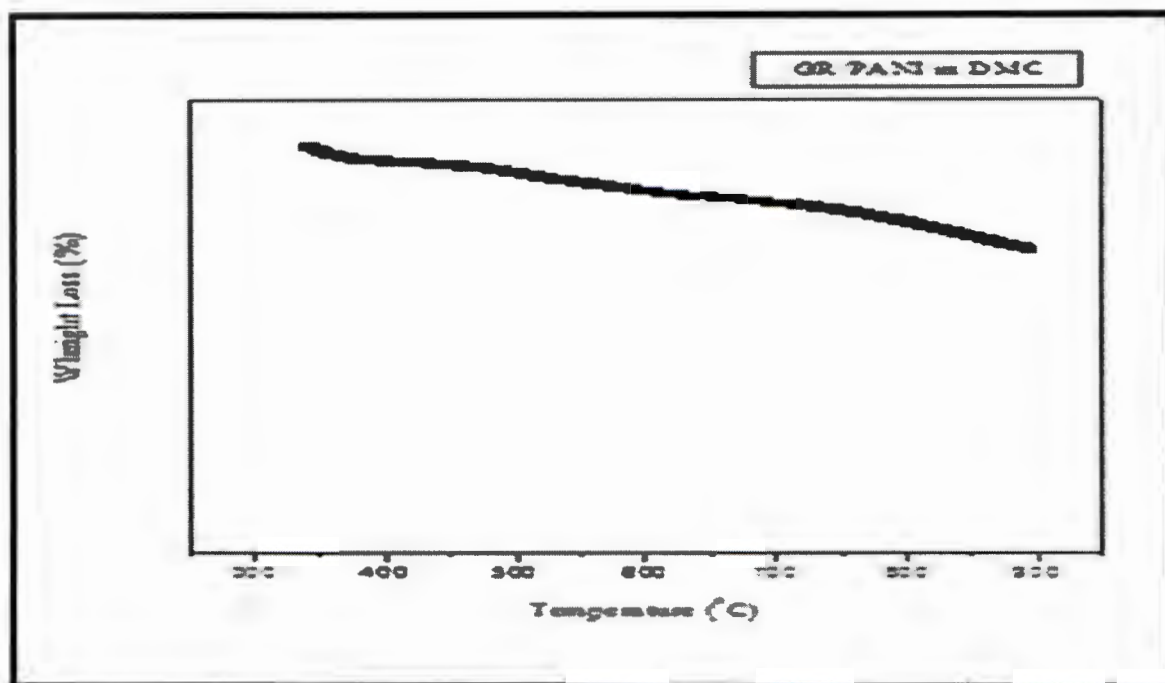


Figure 6.37: TGA graph of GR/PANI in DMC

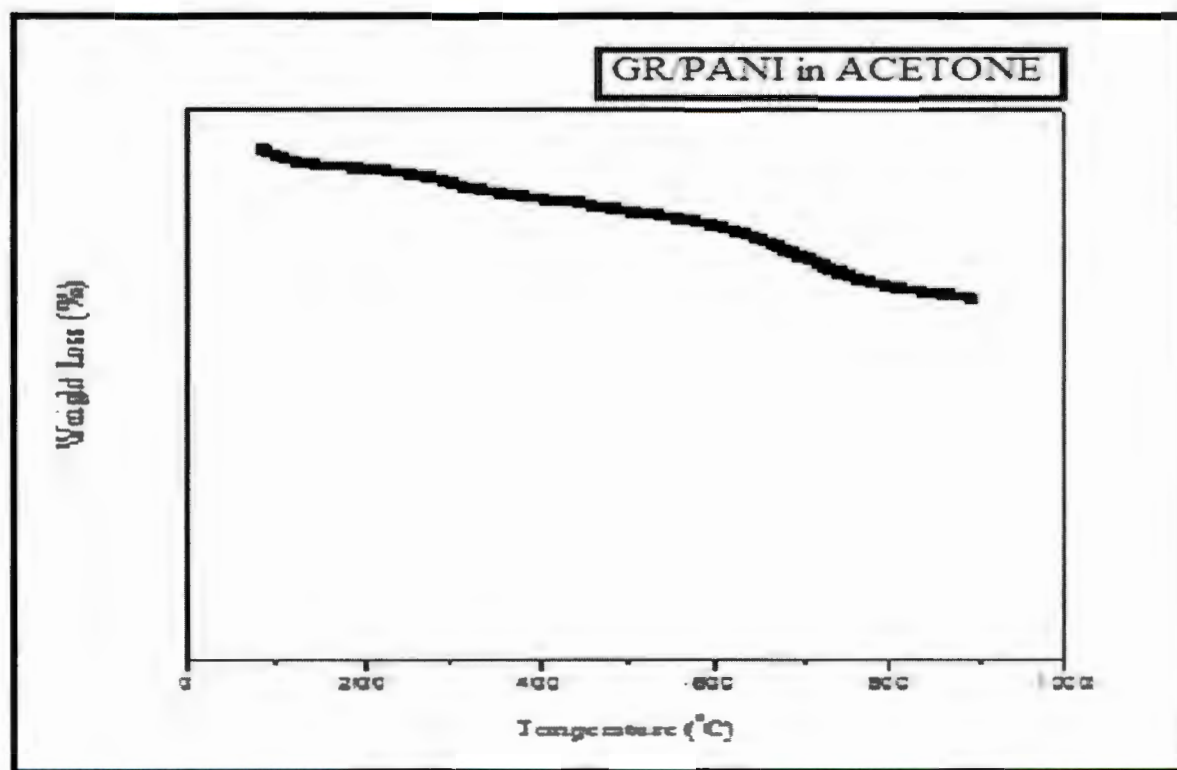


Figure 6.38: TGA graph of GR/PANI in Acetone

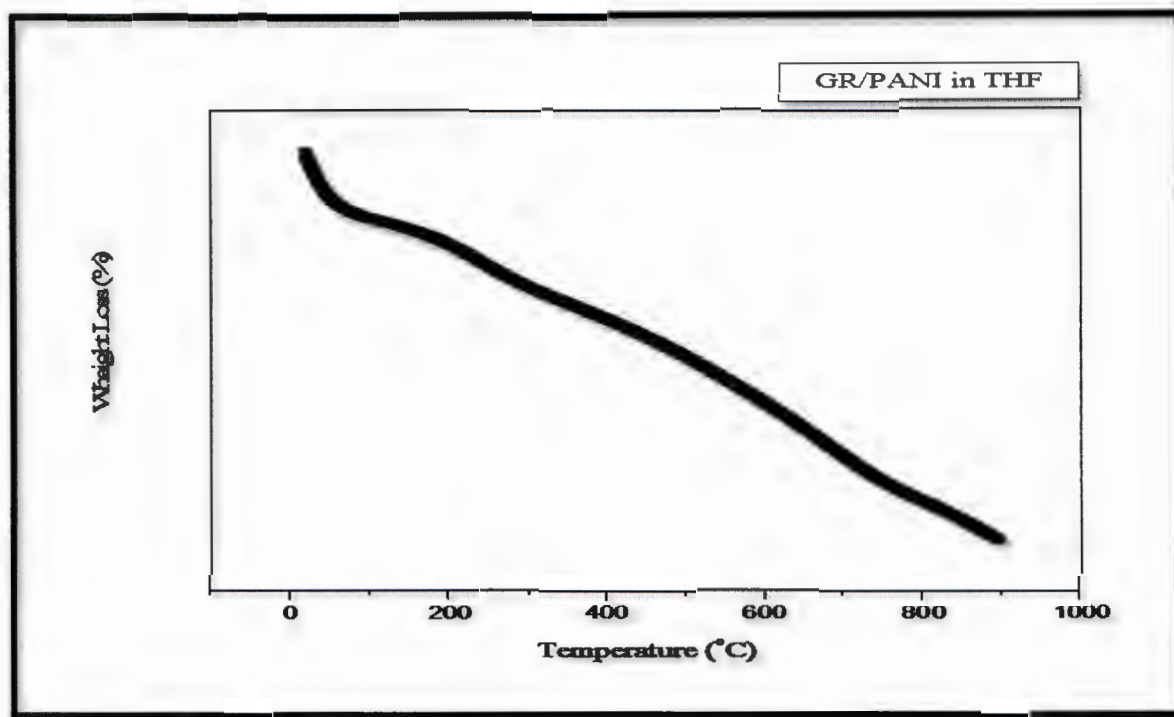


Figure 6.39: TGA graph of GR/PANI in THF

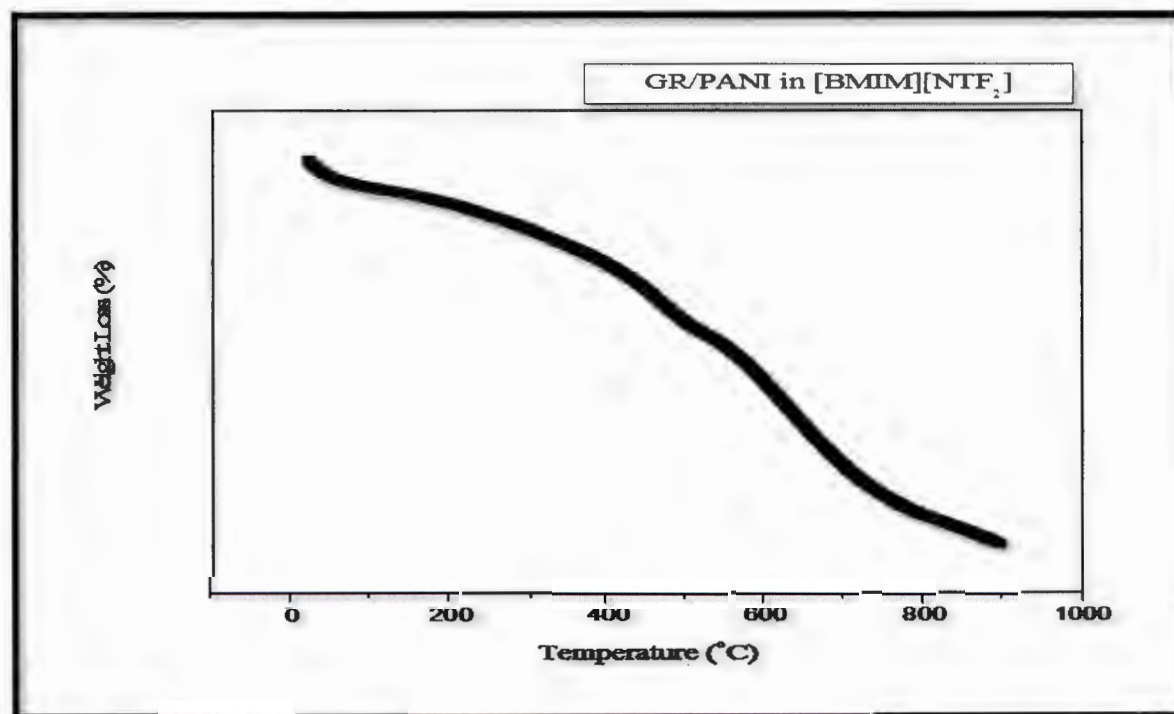


Figure 6.40: TGA graph of GR/PANI in [BMIM][NTF₂]

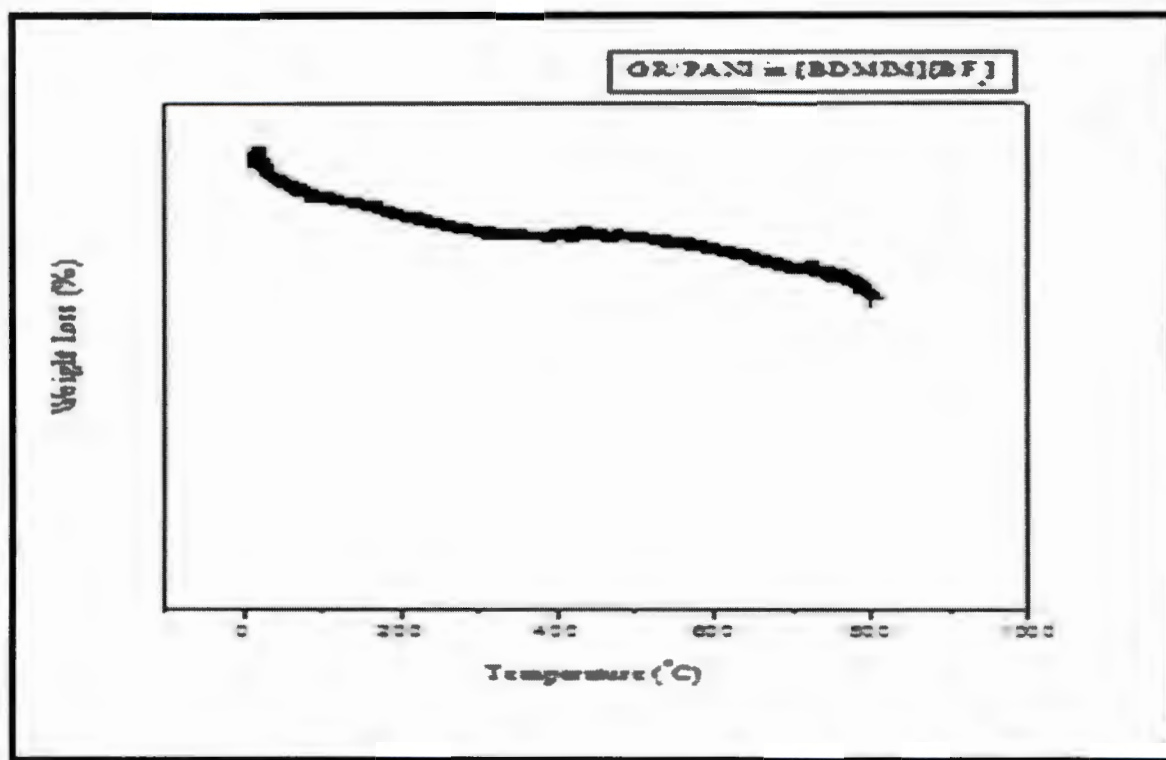


Figure 6.41: TGA graph of GR/PANI in [BDMIM][BF₄]

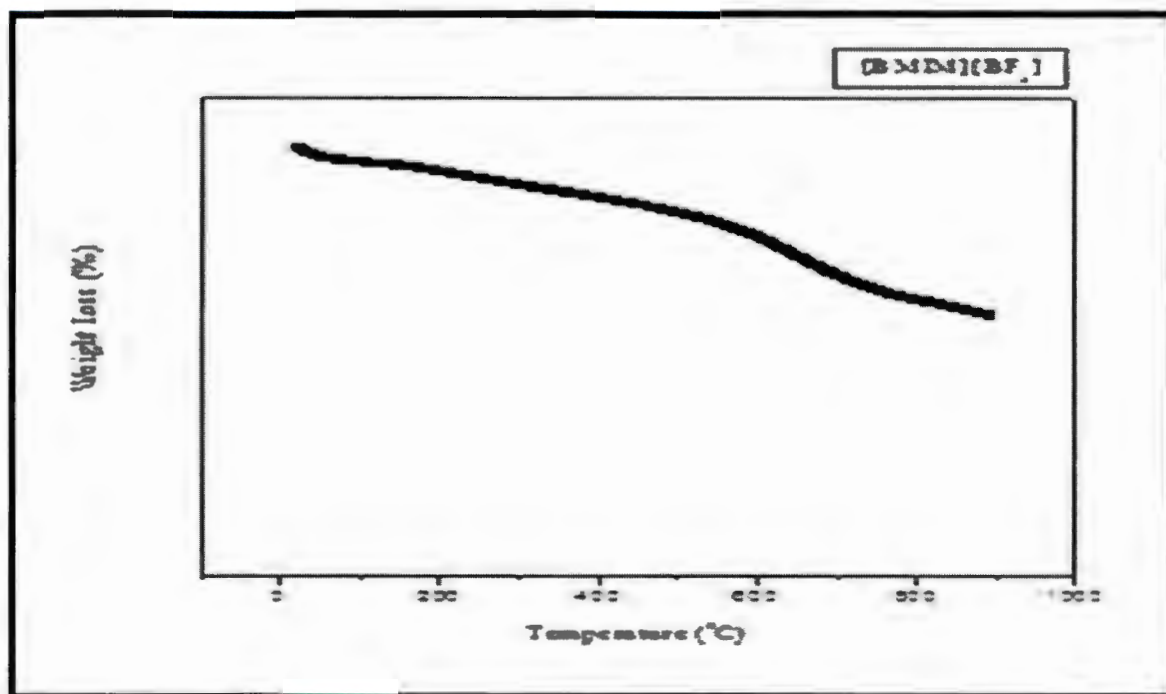


Figure 6.42: TGA graph of GR/PANI in [BMIM][BF₄]

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