Optimization of Preparation Techniques and Dielectric Study of Polyanilines in the Microwave & High Frequency Field

Thesis submitted to the

COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY

by

Rinku Mariam Thomas

In partial fulfilment of the requirements
for the award of the degree of

DOCTOR OF PHILOSOPHY

DEPARTMENT OF POLYMER SCIENCE AND RUBBER TECHNOLOGY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI- 682022

MAY 2005

Certificate

This is to certify that this thesis entitled **"Optimization of Preparation Techniques and Dielectric Study of Polyanilines in the Microwave & High Frequency Field"** is a report of the original work carried out by Smt. Rinku Mariam Thomas under our supervision and guidance in the Department of Polymer Science and Rubber Technology, Department of Electronics and Department of Applied Chemistry, Cochin University of Science and Technology, Kochi-682022, India. No part of the work reported in this thesis has been presented by her for any other degree from any other institution.

Dr. K.E.George
Professor
Dept of Polymer Science and Rubber Technology,
Cochin University of Science and Technology.

Dr. K.T.Mathew
Professor, Dept of Electronics,
Cochin University of Science and Technology.

Dr. S.Prathapan
Reader, Dept of Applied Chemistry,
Cochin University of Science and Technology

Kochi-22
27th May 2005

Declaration

I hereby declare that the thesis entitled **"Optimization of Preparation Techniques and Dielectric Study of Polyanilines in the Microwave & High Frequency Field"** is the original work carried out by me under the supervision of Dr. K. E. George, Professor, Department of Polymer Science and Rubber Technology, Dr. K. T. Mathew, Department of Electronics, Dr. S. Prathapan, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi-682022, and no part of this thesis has been presented by me for any other degree from any other institution.

Kochi-22
27th May 2005

Rinku Mariam Thomas

'For I know the thoughts that I think toward you' Says the Lord, 'thoughts of peace not of evil, to give you a future and hope. Then you will call upon Me and go and pray to Me and I will listen to you. And you will seek Me and find Me, when you search for me with all your heart. I will be found by you, says the Lord and I will bring you back from your captivity'.

JEREMIAH 29:11-14

This thesis is a fulfilment of the dream,

My daddy and amma always cherished.

Coupled with the unfaltering love of my husband

& unstinted support of chechy

ACKNOWLEDGEMENT

Firstly, I thank Dr.K.E.George, my guide and Dr.Rani Joseph, head of the Department of Polymer Science for their acceptance and continuous support during the Ph.D.programme. Rani teacher was always there to listen and to give advice. Together they showed me different ways to approach a research problem and the need to be persistent to accomplish any goal. George sir and Rani teacher have been most compassionate in their approach when any difficulties arose. I specially take this moment to thank Prof.John Kuruvilla for having put in a word of introduction and helped me to take up this research opportunity

I also thank Dr.K.T Mathew and Dr. S.Prathapan my research co-guides for supervising my study on the interdisciplinary topic of research. I thank sincerely for their valuable guidance. Special thanks go to Prathapan sir who is most responsible for helping me bring forth the thesis in a more refined manner. He edited, rewrote, and guided the direction and the content of this whole manuscript.

I thank the Faculty members at PSRT for their best wishes and giving me an opportunity to carry out my research in the department. I wish to thank the Dr.Ratheesh, Seema chechy and the other members of the microwave group at C-Met Thrissur, for allowing me to carry out a major part of my sample measurements. I acknowledge with gratitude the discussions with the group and the suggestions that have helped me fashion my work in a better way.

This thesis sees the light of the day because of my chechy [Dr.Honey John] and her loving family. I remember with immense gratitude, the warmth with which chechy, Josettan, Emmu and Nou have welcomed me to their home. Chechy showed confidence in me when I doubted myself, and brought out the good ideas. Without her prayers, encouragement and constant guidance and the loving care for me, I could not have finished this dissertation. She was always there to think through my problems. I treasure this intimate relationship as a blessing from Above. She has been with me in all the ups and downs in my life at CUSAT. Chechy's family at Kothamangalam has supported me immensely with their incessant prayers and good wishes, My love and respect to them.

My dearest Nisha, she has been my constant companion in words, thought and deeds. She sensed my every need and thought without clarifications. Words fail me when I wish to wrap up the relationship. She was a perennial source of love and support in my life. My thanks to Radhakrishnan, for his presence and support in the final phase of my research life.

My special thanks to Dr.Joe Jacob, for reading through the manuscript. His encouragement and support has been most gratifying.

I would like to thank the rest of the research fraternity at PSRT Dr.Ushamani, Litty chechy, Lovely teacher, Jose sir, Aswathy, Thomas, Anoop, Bipin and Rajesh for their friendship, encouragement and gave insightful comments. Thank you, Soney sir for carrying out the SEM analysis of my samples inspite of the busy schedule. I owe a word of gratitude Dhanya for helping carry out the analysis of many of my samples. The office team at PSRT has helped me to cruise through the official hurdles. My special gratitude to Mr. Bakker, for his goodwill and words of advice in official matters. Thanks to a short yet memorable acquaintance with Saritha, Maya Teacher, Jude sir and the other new faces in the department..

My dear friends back at the Athulya Hostel have encouraged me a lot to put this on paper. My roommate and friend, Teny deserves a special mention. Her discipline and devotion to research has left me impressed and motivated. Ambily, Beena, Ishwarya Kochurani, Maya, Pravitha, Radhika, Sr.Ritty, and Rehna have helped maintain that affable environment and share a lighter moment in the midst of the research life. I carry back with me the pleasant memories of my stay at Athulya. Sreelu has always maintained the relationship through her short yet frequent e-mails.

This more personal account is mine alone. I dedicate this effort to my husband who suffered through these three years, and who has given me the love, encouragement, and devotion which has enriched and fulfilled my own life. To our wonderful family, pappa and amma who have accepted me without bias, this thesis is also dedicated.

Last, but not least, I thank my daddy, amma and Rekha for their love, prayers and dreams. They have educated me with aspects from all facets of life offered me unconditional support and encouragement to pursue my interests.

And, finally, it is dedicated halo of love by which I am surrounded, through which God has made his Presence Known in my life. I praise God for His Infinite Mercy

Rinku Mariam Thomas

PREFACE

The synergy between the electrical and mechanical properties of polymers has opened up a realm of material science that was less explored and hence less exploited until date. Not all polymers behave the same when subjected to voltage and plastics can be classified as 'polar' or 'non-polar' to describe their variations in behavior. In polar plastics, permanent dipoles are created by an imbalance in the distribution of electrons and in the presence of an electric field the dipoles will attempt to move to align with the field. This will create 'dipole polarization' of the material. However, for both polar and nonpolar polymers, dielectric breakdown can occur at sufficiently high voltages to give current transmission and possible mechanical damage to the plastic.

Ideal dielectrics consist of no polarizable bonds and no delocalized electrons. In addition, they have mobilities of zero for any free charge applied to their surface and thus are insulators. Typically, structural and/or compositional modifications change the dielectric constant and the dissipation factor of a polymer in the same direction. By taking advantage of the structural dependence of these dielectric properties, polymers can be tailor-made to suit a specific application by controlling the reactive end groups, introducing polar structural moieties, and changing the curing mechanism. However, these three factors must be balanced with the processability, thermal stability, mechanical properties etc.

Apart from the conventional polar and nonpolar polymers that are poor conductors of electricity, a new generation of intrinsically conducting polymers are currently available. Polymers such as polyanilines, polyacetylene, polythiophene and polypyrrole belong to this category. Most of these are characterized by a π-conjugated backbone. π-conjugated polymers are characterized by an alternation of single and double bonds and are typically semiconductors in their neutral state. The discovery that these plastics can reach metallic conductivities when charges are introduced along the backbone led to a major breakthrough in the area of functional plastics. The intriguing behavior of π-conjugated compounds originates from their intrinsic properties and from the modification of these properties. Intrinsically conducting polymers such as Polyaniline exhibit unusually high polarisability and high dielectric constant, which extends into microwave range.

These materials offer the prospect of combining novel electronic properties with the ease of processing and their properties can be tuned by chemical modification to give desired features. It is contemporary to assess the effect of synthesis conditions on the morphology and dielectric properties of conducting polymers.

This work is devoted to the preparation and dielectric characterization of Polyaniline and its analogues in ISM band frequency of 2-4 GHz that includes part of the microwave region (300 MHz to 300 GHz) of the electromagnetic spectrum and an initial dielectric study in the high frequency [0.05MHz-13 MHz]. Polyaniline has been synthesized by an *in situ* doping reaction under different temperature and in the presence of inorganic dopants such as HCl, H_2SO_4, HNO_3, $HClO_4$ and organic dopants such as camphorsulphonic acid [CSA], toluenesulphonic acid [TSA] and naphthalenesulphonic acid [NSA]. The variation in dielectric properties with change in reaction temperature, dopants and frequency has been studied. The effect of codopants and microemulsions on the dielectric properties has also been studied in the ISM band. The ISM band of frequencies (2-4 GHz) is of great utility in Industrial, Scientific and Medical (ISM) applications. Microwave heating is a very efficient method of heating dielectric materials and is extensively used in industrial as well as household heating applications.

Contents of the thesis:

The thesis consists of 7 chapters.

Chapter 1: presents a comprehensive introduction on conducting polymers. It also includes a review of the most relevant reports pertaining to the field of work. The scope and objective of the present investigation is summarized

Chapter 2: deals with the materials used and the experimental procedures adopted for the study

Chapter 3: Chapter 3 is divided in to three parts. The effect of preparation temperature, different dopants [inorganic and organic] and concentrations of dopants on the dielectric properties of polyaniline samples are described in Part I. The characterization using IR spectroscopy, TGA, DSC and SEM is also included in this part. It also deals with the preparation, characterization and dielectric property study of polyaniline in the undoped state. A detailed comparison of the dielectric properties of undoped PAni, $HClO_4$ and CSA doped samples is included. The synthesis and the dielectric properties of a few analogues of polyaniline such as poly(*o*-toluidine) [PoT] and poly(*o*-anisidine) [PoAn] is described in Part II. The effects of variation of preparation temperature and dopants [inorganic and organic] on the dielectric response of the conducting systems have been carried out in the ISM band of 2GHz - 4GHz. A comparison of the dielectric properties of the different matrices is also included. The study reveals the suitability of $HClO_4$ as an effective dopant among the inorganic dopants. The dielectric behavior of polyaniline prepared in the doped [inorganic and organic] and undoped condition in the high frequency field of 0.05MHz - 13MHz are evaluated in Part III.

Chapter 4: Chapter 4 is divided in to three parts. The morphological changes in the presence of chiral sugars as codopants along with organic sulphonic acids are dealt with in Part I. The study has been carried out for polyaniline and poly(*o*-toluidine). Among the organic dopants used, β-naphthalenesulphonic acid [β - NSA] imparted a tubular morphology to polyaniline. A detailed characterization of the microtubules was carried out using IR spectroscopy, thermal analysis, SEM analysis and XRD analysis. Part II deals with the synthesis, characterization and dielectric study of PAni prepared via an emulsion polymerization pathway. The SEM characterization reveals a uniform morphology in the conducting system. A detailed comparison of the dielectric properties of the samples is also included in each section. A separate section on the high frequency field measurements [0.05-13MHz] is included in Part III. The parameters like dielectric constant, loss tangent and conductivity were studied.

Chapter 5 Part I presents the study of composites of the conducting polymer with polyvinyl chloride[PVC] and three grades of silica in different ratios.. Part II deals with the synthesis and characterization using SEM of composites with three grades of silica. Various dielectric properties like dielectric constant, dielectric loss, absorption coefficient etc. are described.

Chapter 6 is divided in to two parts. A detailed comparison of the best matrices from each section of the thesis was selected and the trends are discussed in Part I. PAni undoped shows variation in dielectric constant with change in frequency. This material shows prospects of steering the beam when a voltage is applied to the sample. This is achieved due to the change in velocity of the beam, which causes a phase shift, allowing the beam to be steered through a deflected angle. An application-oriented study based on the beam steering property of the conducting system is included in Part II of this chapter

Chapter 7 gives the summary and conclusions of the work.

At the end of each chapter a list of pertinent references is given. A list of abbreviations used in this thesis is also cited.

CONTENTS

Chapter 1: Introduction

Chapter 2: Experimental Techniques

Chapter 3: Optimization of Preparation conditions on the dielectric properties of Polyaniline

Chapter 4 : Effect of preparation techniques on the Morphology and Dielectric properties of Polyanilines

Chapter 5: Studies on Polyaniline composites

Chapter 6: Comparative and applications study

Chapter 1

General Introduction

1.1 THE WORLD OF MATERIALS

Today science is close to fulfilling a dream : assembling molecules together with great precision and reliability to create new materials with nearly any desired capabilities or characteristics. Like the typesetter of a century ago, materials scientists can construct materials, molecule by molecule, to meet a specific application or create a desired capability. This is particularly true in the case of conjugated polymers that have, off late, become favourite tinker toys for chemists and technologists. During the past 25 years, several classes of synthetic materials have been developed and explored in detail by chemists and physicists. However, the polarization between mainstream synthetic organic chemists and polymer chemists severely hampered the progress in developing modern polymer-based materials. More damagingly, the interest in these materials was fluctuating during this period. Recently there has been a revival of interest in the construction of well-defined macromolecules [1-3]. This was inevitable due to their emerging large-scale applications in the development of electro-optic devices such as light emitting diodes (LED), field effect transistors (FET) and photovoltaic (PV) devices. As a result, modern synthetic chemistry has attained widespread utility in the construction of these classes of compounds. This renewed interest fruitfully bridged the disciplines of synthetic organic chemistry and polymer chemistry. The de novo synergy between polymer chemistry and synthetic organic chemistry has produced thousands of published papers, patents, and conference communications.

1.2 HISTORICAL PERSPECTIVE

1.2.1 Conductive polymers - a surprising discovery

We conceptualise polymers - that is, plastics - being somehow the opposite of metals. Our stock response about polymers is that: they insulate, they do not conduct electricity. Electric wires are coated with polymers to protect them - and us - from short-circuits. Yet Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa have changed this perception with their discovery that a polymer, polyacetylene, can be made conductive almost like a metal. Polyacetylene was known since 1974 when it was prepared as a silvery film by Shirakawa and co-workers from acetylene, using a Ziegler-Natta catalyst (K. Ziegler and G. Natta, Nobel Prize in Chemistry 1966). But despite its metallic appearance it was not a conductor. In 1977, however, Shirakawa, MacDiarmid and Heeger discovered that oxidation with chlorine, bromine or iodine vapour called 'doping' made polyacetylene films 10^9 times more conductive than the virgin polymer[4]. The "doped" form of polyacetylene had a conductivity of 10^5 Siemens per meter, which was higher than that of any previously known polymer. As a comparison, teflon has a conductivity of 10^{-16} Sm^{-1} and silver and copper 10^8 Sm^{-1}. A key property of a conductive polymer is the presence of conjugated double bonds along the backbone of the polymer. In addition to conjugation, charge carriers in the form of extra electrons or "holes" have to be incorporated into the material.

For most of the 20th century, research on the electrical properties of organic solids has been a matter of merely academic interest: it was commonly believed that molecular materials could not compete with 'conventional' metals and semiconducting materials. The last decades witnessed significant progress, associated with the development of novel polymer-based materials exhibiting interesting electrical and optical properties, which could be applied in electronics and photonics. Today conductive plastics are being developed for many uses, such as in corrosion inhibitors, compact capacitors, antistatic coatings, electromagnetic shielding of computers, and in "smart" windows that can vary the amount of light they allow to pass, etc. A second generation of electric polymers has also appeared in, e.g., transistors, light-emitting diodes, lasers with further applications as flat television screens, solar cells, etc. Polymers have the potential advantages of low cost and that they can be processed, e.g., as films. We may soon be seeing electroluminescent plastics papered on walls for illumination.

1.2.2 The Chronological Ladder

Conjugated polymers are organic semiconductors (and, possibly, organic conductors) and as such interesting in a wide variety of optical, electronic, optoelectronic, and sensory applications including light emitting diodes, thin film transistors, photovoltaic cells and plastic lasers, to name a few. Unlike simple polymers, a π-conjugated polymer has a chain of alternating single and double or single and triple bonds. The energy of the π -electrons in both double and triple bonds is much higher than the energy of the electrons in single bonds. The energy gap, which is very large for an insulator, is much smaller for a material that has an alternating pattern of single-double or single-triple bonds, in other words, a π-conjugated polymer. Once we realize that π-conjugated polymers are semiconductors, the obvious question is whether we can make this whole spectrum of devices, which we normally do with silicon, gallium arsenide, or other inorganic semiconductors, with π-conjugated polymers? The answer is "yes." An organic polymer that possesses the electrical, electronic, magnetic and optical properties of a metal while retaining the mechanical properties, processibility etc. of a typical polymer is termed an 'intrinsically conducting polymer' (ICP) more commonly known as a 'synthetic metal'. Conjugated polymers are quasi-one dimensional systems owing to their strong intra-molecular interactions and rather weak inter-molecular interactions. As a consequence, electron-electron interactions are weakly screened, and thus both electron-electron interactions and electron-lattice coupling are fundamentally important in determining the electronic behavior. Together, they determine the relative ordering of the electronic states, and this, in turn, determines the optical properties of conjugated polymers.

As early as 1862 H. Letheby of the College of London Hospital, by anodic oxidation of aniline in sulphuric acid, obtained a partly conductive material, which was probably polyaniline. In the early 1970s, it was found that the inorganic explosive polymer, poly(sulphur nitride) (SN)x, was superconductive at extremely low temperatures (Tc = 0.26 K). Many conductive organic compounds were also known, such as those discovered by K. Bechgaard (Copenhagen) together with D. Jerome (Paris) and famous for being superconductive at rather "high" temperatures (Tc around 10 K).

However, polyacetylene[4-7] was the conductive polymer that actually launched this new field of research. Excellent review articles in this regard have been published by Feast, *et al*[8] and M.G.Kanatzidis[9].

Natta and co-workers[10] prepared polyacetylene in 1958 by polymerising acetylene in hexane using $Et_3Al/Ti(OPr)_4$ (Et = ethyl, Pr = propyl) as a catalyst. In the early 1970s Shirakawa and co-workers[11] adapted the method to make well-defined films of polyacetylene. Shirakawa's procedure also allowed silvery all-trans-polyacetylene to be formed by running the reaction in *n*-hexadecane at $150^{\circ}C$. Their conductivity was relatively modest: *cis*-polyacetylene 10^{-5}-10^{-7} Sm^{-1} and *trans*-polyacetylene 10^{-3}-10^{-2} Sm^{-1}.

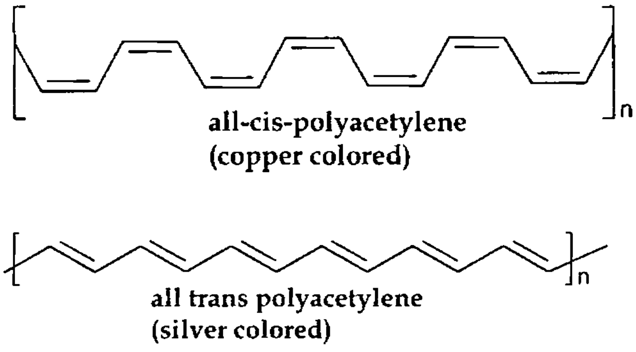


Figure 1.1: The cis and trans forms of polyacetylene

In 1975 Alan Heeger and Alan MacDiarmid collaborated to study the metallic properties of a covalent inorganic polymer, $(SN)_x$. The collaboration between Shirakawa and MacDiarmid on further research in polyacetylene led to more interesting results, such as the dramatic increase in conductivity of polyacetylene by a factor of 10^{11} when doped with AsF_5. The seminal paper received for publication on May 16, 1977, had the title: Synthesis of electrically conducting organic polymers: Halogen derivatives of polyacetylene $(CH)_x$[5]. The high conductivity found by Heeger, MacDiarmid and Shirakawa clearly opened up the field of "plastic electronics". Other polymers studied extensively since the early 1980s include polypyrrole, polythiophene (and various polythiophene derivatives), polyphenylene vinylene and polyaniline.

Polyacetylene remains the most crystalline conductive polymer but is not the first conductive polymer to be commercialised. This is because it is easily oxidised by the oxygen in air and is also sensitive to humidity. Polypyrrole and polythiophene differ from polyacetylene most notably in that they may be synthesised directly in the doped form and are very stable in air. In addition to improved environmental stability, these polymers differ from $(CH)_x$ by (i) their non-degenerate ground state, which has important consequences regarding the nature of the charged species involved in the mechanisms of charge transport[12] and (ii) by their electrochemical synthesis which leads in one step to a doped conducting polymer. Their conductivities are low, however: only around 10^2-10^4 Sm^{-1}, but this is enough for many practical purposes. These polymers have the advantage of relatively high stability and processibility, *e.g.* poly (3-dodecylthiophene), can be prepared as a melt-spun, strong film in the undoped state and then doped to a conductivity of 10^5 Sm^{-1}.

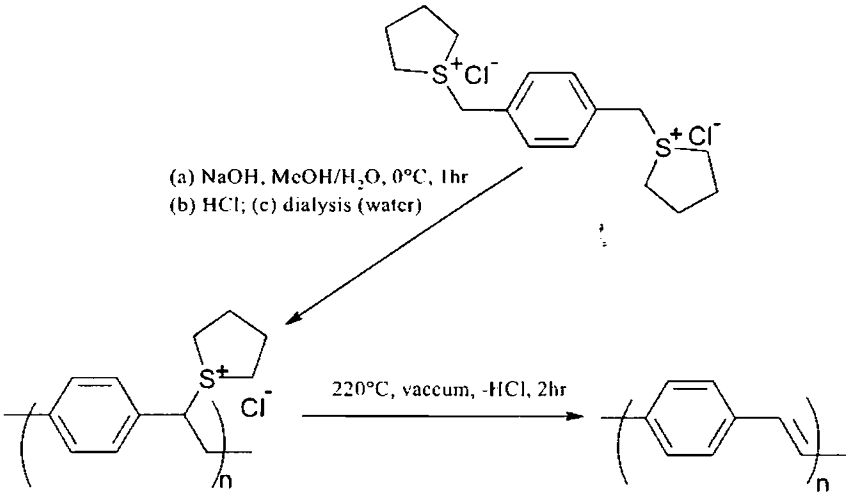
1.3 SYNTHESIS AND PROCESSING

Modern synthetic organic and organometallic methodologies are proving to be extremely powerful for the direct acquisition of the desired compounds by stepwise approaches. Although the specific systems covered in the section below will be conjugated molecules, the general methods of preparation described in this section are applicable to the synthesis of both conjugated and nonconjugated systems. Current interest in conducting polymers [CPs] started in the late 1970s with the discovery of electrical conductivity in oxidatively doped polyacetylene $(CH)_x$[13,14]. In the wake of this pioneering work, new classes of CPs based on aromatic precursors such as pyrrole[15,16], benzene[17], aniline[18], or thiophene[19,20] have been developed thus contributing to extending their potential practical applications. During the past 20 years these CPs have given rise to an enormous amount of experimental and theoretical work devoted to (i) the analysis of their structure and properties using a whole arsenal of physical techniques, (ii) the development of synthetic methods allowing a better control of their structure and electronic properties, (iii) the synthesis of functional polymers in which the electronic properties are associated with specific properties afforded by covalently attached prosthetic groups[20,21,22] and (iv) the analysis of their multiple technological applications extending from bulk utilizations such as antistatic coatings, EMI shielding or energy storage, to highly sophisticated electronic, photonic and bioelectronic devices.

1.3.1 Synthesis

[i] Conjugated Polymers from Non-conjugated Precursor Polymers

Poly (p-phenylenevinylene) PPV is the most studied conjugated polymer for electroluminescence (EL) emission[23,24]. The most common method to prepare PPV is the so-called Wessling route from the sulphonium precursor polymer (Scheme 1)[25].



Scheme 1 : Synthesis of PPV

While PPV prepared by the sulphonium precursor route is an intractable material with a rigid-rod microcrystalline structure, the precursor polymer is solution processable and can be converted into the conjugated structure, for example, by thermal treatment.

[ii] Conducting Poly dienes

In 1988, Thakur reported that the conductivity of non-conjugated *cis*-1,4-polyisoprene (i.e., natural rubber) could be increased by about ten orders of magnitude upon doping with iodine[26]. In view of the ease with which conducting rubber can be made and the potential challenge of Thakur's claim to modern theory of conducting polymers, Thakur's report received complimentary comments from several scientific journals[27]. Meanwhile, various other polymers with isolated (non-conjugated) double bonds, such as *trans*-1,4-polyisoprene, 1,4-poly-(2,3-dimethylbutadiene), and *trans*-1,4-

polybutadiene, were also found to turn dark in colour and conductive when doped with iodine in the solid state. Surprisingly, however, *cis*-1,4-polybutadiene did not change colour or become conductive upon I_2-doping under the same conditions[27,28]. Dai and White[28] were the first to demonstrate that I_2-doping of 1,4-polyisoprene produces conjugated sequences of unsaturated double bonds in the polyisoprene backbone through polar addition of I_2 into the isolated double bonds in the polymer chain, followed by HI elimination. In view of these results, it is clear that the alleged conductivity of "doped" natural rubber as discovered by Thakur is due to simple chemical modification of polyisoprene structure to polyacetylene-type structure.

1.3.2 Processing

There is often a barrier between the first chemical synthesis of a molecular substance and the development of processing methods for its practical applications. Processing polyacetylene and many other polymers such as polypyrrole and polythiophene was for a time ruled out because of their failure to melt or to dissolve in any solvent. Ingenious methods developed over the years have, however, made processing possible. In 1980, James W. Feast and co-workers at the University of Durham synthesised polyacetylene from a soluble precursor polymer, poly(7,8-bis(trifluoromethyl)- tri cyclodeca(3,7,9-triene). Upon heating, the dissociation product bis-trifluoromethylbenzene evaporated off to leave a polyacetylene film, which is much denser than Shirakawa's material. Another important invention was Caltech researchers Robert H. Grubbs' and co-workers' production of polyacetylene by metathesis polymerisation of cyclooctatetraene in the presence of a titanium alkylidene complex as catalyst. Grubbs' polyacetylene reportedly had a conductivity of about 35,000 Sm^{-1}, but was as intractable and unstable as other polyacetylenes. However, by attaching alkyl substituents to the cyclooctatetraene molecule, Grubbs and his group managed to prepare a soluble substituted polyacetylene that could be cast in any desired form, although the alkyl substituents seemed to lower the conductivity considerably. Another advance in electrical properties, but unfortunately not in processbility, came in 1987 when BASF (Badishe Anilinen und Soda Fabrik) scientists Herbert Naarman and Nicholas Theophilou in West Germany developed a polymerisation method based on Shirakawa's method, at 150°C. When doped, their material was claimed to have a conductivity of more than 10^7 Sm^{-1}, *i.e.*, of the same order as that of Copper's. This polyacetylene may have a higher conductivity because of its greater order and fewer defects than previous preparations. Other polymers with interesting properties have been developed: added to those already listed are polyparaphenylene, polyparaphenylenevinylene, polypyrrole, polythiophene and polyaniline and their derivatives. These materials generally show much lower conductivity than polyacetylene, ca 10^2–10^4 Sm^{-1}, which is adequate for many purposes.

[i] Soluble Conjugated Polymers by Copolymerization

Copolymerization of conjugated polymers with various soluble segments provides another effective method to circumvent the intractability of conjugated polymers. The combination of optoelectronic properties characteristic of conjugated structures and the solubility of soluble polymeric segments in a single copolymer chain should, in principle, lead to a material with properties characteristic of both of the constituent components. In most cases, the integrity of conjugated structures and accompanying desirable properties of conjugated polymers can largely be preserved by making block or graft copolymers with suitable conventional polymer blocks.

[ii] Block and Graft Copolymers

It now appears that polyacetylene may be solubilized by making copolymers with polyisoprene, polybutadiene, or polystyrene via the so-called anionic to Ziegler-Natta route[29-32]. Using $Ti(OBu)_4/AlEt_3$ as a catalyst, Bates and Baker[29] ,Aldissi,[30] and Galvin and Wnek[31] have successfully copolymerized acetylene onto polystyrene, 1,4-polybutadiene, and 1,4-polyisoprene chains to produce block copolymers. It is noted that polyacetylene chains in the block copolymers synthesized using the Shirakawa-type titanium catalyst exist in the trans form. Using a novel Luttinger-type cobalt catalyst system[33]. Armes et al[31] and Dai and White[32] have successfully synthesized block copolymers of poly(1,4-dienes) and polyacetylene. Graft copolymers of polyacetylene and polyisoprene, polybutadiene, or polystyrene have also been prepared via similar reactions[32]. It was found that polyacetylene chains in the block and graft copolymers made using cobalt catalyst are mostly in the cis form due to the low temperature nature of the copolymerization reaction, and because isomerization of the *cis*-polyacetylene segments was retarded by some intramolecular barriers (e.g., the chemically bonded polyisoprene chains), making the cis isomer rather stable at room temperature[32]. A Wittig-type coupling PPV derivatives is attractive for fabricating water soluble electroluminescent displays by ink-jet printing technologies These PPV derivatives with polar side groups are very useful for applications in light-emitting electrochemical cells (LECs).

[iii] Hyper branched Conjugated Polymers

Another interesting area closely related to the block and/or graft conjugated copolymers is the synthesis of hyperbranched/dendritic (starburst) super molecules with conjugated moieties. Dendritic macromolecules are molecular species with a large number of hyperbranched chains of precise length and constitution surrounding a central core[34]. The ability to control placement of functional groups and to construct unique microenvironments within dendritic macromolecules has attracted a wide range of potential applications, including drug delivery[35] rheology control[36] and molecular electronics[37]. Although the synthesis of fully conjugated dendritic macromolecules is not straightforward, a few reports have appeared[37]. Preliminary spectroscopic and conductivity measurements indicated that the as-synthesized hyper-branched conjugated polymers show relatively strong fluorescence emission and can form multi-dimensional structures with relatively high conductivities (ca. 10 ± 3 Scm^{-1}) after doping. The hyper-branched conjugated polymers thus prepared are soluble in most common organic solvents, including chloroform, dichloromethane, tetrahydrofuran (THF), and ethyl acetate.

1.4 MECHANISM OF POLYMER CONDUCTIVITY

1.4.1 Valence band theory

In metals, there is a high density of electronic states having electrons with relatively low binding energy, and "free electrons" move easily from atom to atom under an applied electric field. The conductivity of metals measured with standard procedures shows a value of around 10^8 Sm^{-1}. The electrical properties of a material are determined by its electronic structure. In a metal, the orbitals of the atoms overlap with the equivalent orbitals of their neighbouring atoms in all directions to form molecular orbitals similar to those of isolated molecules: With N interacting atomic orbitals we will have N molecular orbitals and N will be a very large number (typically 10^{22} for a 1 cm^3 piece) in the case of metals. Many molecular orbitals spaced together in a given range of energies, can form an apparently continuous band of energies (Figure 1.2). In a metal atom the valence orbitals are not filled. Thus the band of N molecular orbitals will not be filled either, but at a certain energy level all molecular orbitals above this level will be empty. The conductivity of the metal is due either to only-partly-filled valence [highest occupied] or conduction bands [lowest unoccupied], or due to the band gap being near zero, so that with even a weak electric field the electrons easily redistribute: electrons at higher energy and holes at lower energy, this situation is ideal for rapid transport of a charge: An electron injected at a certain position into a conduction orbital, which is delocalised over macroscopic dimensions, could leave the same orbital instantaneously at any other point in that orbital's space.

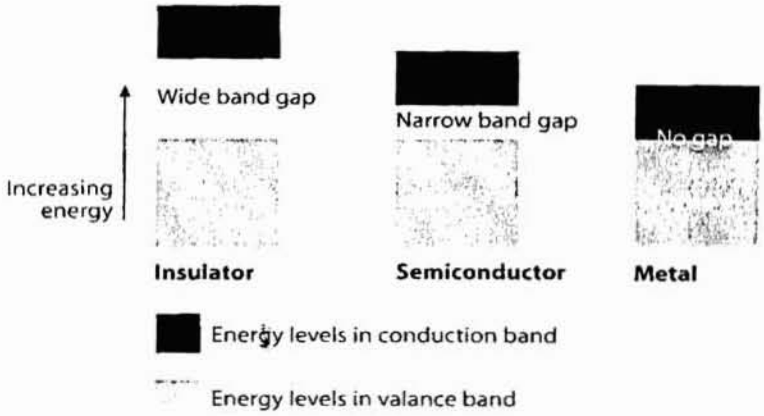


Figure 1.2: Simple band picture explaining the difference between an insulator, a semiconductor and a metal.

1.4.2 Molecular orbital theory

A simple free-electron molecular orbital model provides the minimum elements needed for describing quantitatively a conductor, semiconductor or insulator built up of a linear chain of atoms such as in polyacetylene. Assume a row of N atoms separated by a distance *d*, so the total length of the chain is (N-1)*d* or, for large N, approximately N*d*. According to the quantum-mechanical model for a free particle in a one-dimensional box (potential zero inside the box and infinity outside) the wave functions (Figure) correspond to a ladder of eigen values

$$E_n = n^2h^2/8\,m(Nd)^2\text{, with } n = 1,2,3\dots, \qquad (4)$$

where h is Planck's constant, m the electron mass and n a quantum number

If we assume that the π-electrons from the N p-orbitals are filled into this ladder, with two electrons per molecular orbital (according to the Pauli principle), the highest occupied molecular orbital (HOMO) has the energy:

$$E\text{ (HOMO)} = (N/2)^2h^2/8\,m(Nd)^2 \qquad (5)$$

And the lowest unoccupied molecular orbital has the energy:

$$E\text{(LUMO)} = (N/2 + 1)^2h^2/8\,m(Nd)^2 \qquad (6)$$

The energy required to excite an electron from HOMO to LUMO is thus:

$$\Delta E = E\text{(LUMO)} - E\text{ (HOMO)}$$

$$(N+1)h^2/8\,m(Nd)^2 \approx [h^2/8\,md^2]/N \text{ for large N} \qquad (7)$$

Obviously the band gap is predicted to decrease with increasing polymer length, and will thus practically vanish for macroscopic dimensions.

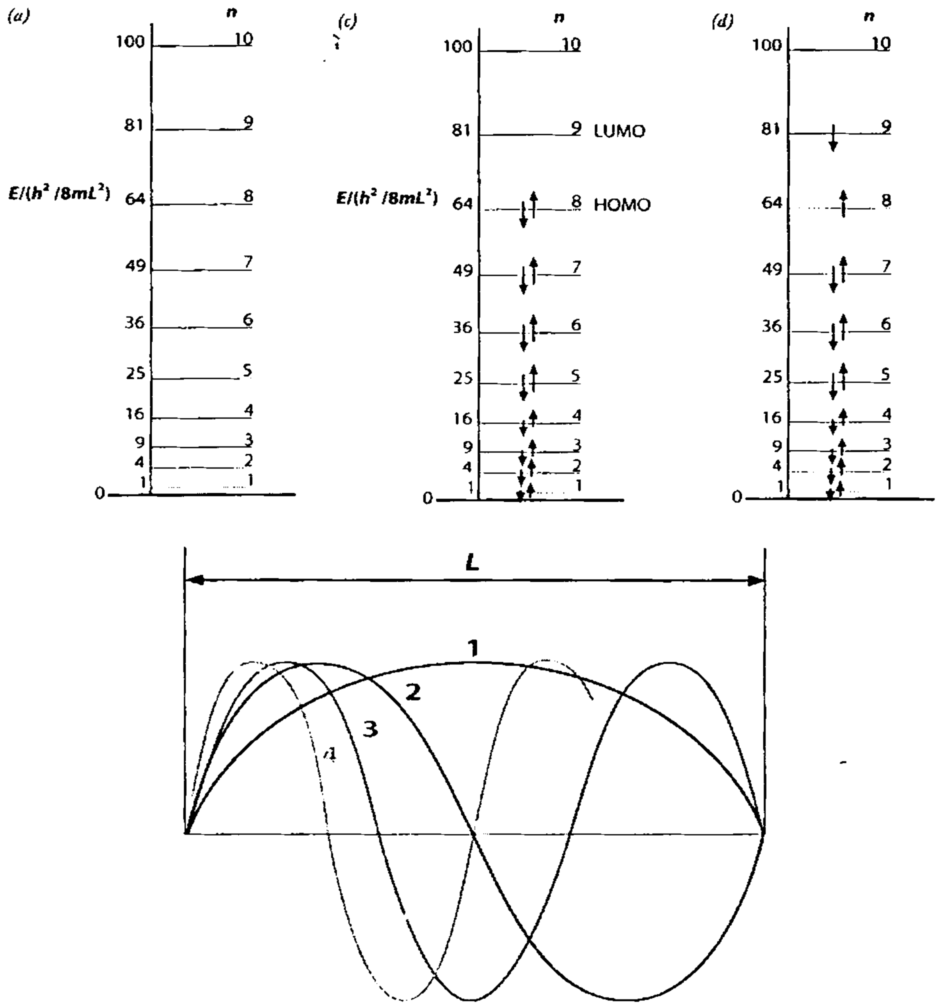


Figure 1.3: Free-electron model (one-dimensional box, length L): energy levels (a) and wave functions (b).

If an electron from one of the filled molecular orbitals is moved up into one of the empty molecular orbitals (Figure 1.3), there is an excited electron configuration and a corresponding *excited state* with energy higher than that of the *ground state.* The minimum energy difference between ground state and excited state - the band gap - corresponds to the energy needed to create a charge pair with one electron in the upper (empty) manifold of orbitals and one positive charge or "hole" in lower (filled) manifold. If the spin of the remaining lone electron in the lower orbital and that of the excited electron are opposite to each other, so that S is still zero ($S = ½ - ½ = 0$), the excited state is a *singlet* state (not magnetic) whereas if the two spins are parallel, $S = ½ + ½ = 1$, the state is said to be a *triplet* state (paramagnetic, *i.e.*, the molecule has a permanent magnetic dipole moment due to electron spin). In the primitive free-electron concept, the band gap would vanish for a sufficiently long chain. Polyacetylene would, thus, be expected to behave as a conductor. Experimentally, the band gap is related to the wavelength of the first absorption band in the electronic spectrum of the substance. Thus a photon with wavelength λ can excite an electron from HOMO level to LUMO if the energy condition is fulfilled:

$$\Delta E = E\,(\mathrm{LUMO}) - E\,(\mathrm{HOMO}) = h\upsilon = h\,c\,/\lambda, \qquad (8)$$

where h is Planck's constant and v the frequency of light (the third equality comes from $v = c/\lambda$ where c the velocity of light). For conjugated polyenes the wavelength of the absorption increases with increasing conjugation: the band gap ΔE decreases with increasing number of double bonds and consequent extension of conjugations.

1.4.3 *Molecular electron-transfer theory*

Electron transfer (ET) reactions, which are also redox reactions, are among the most common and simple chemical reactions. In ET reactions, the electron donor is oxidised and the acceptor is reduced. The free energy that drives the reaction is the difference in reduction potentials between donor and acceptor.

ET is possible between two ground state species or a ground state species and an excited species. The latter process termed photoinduced electron transfer is widely observed. For example, in photosynthesis a series of ET reactions all start from a photo-induced charge separation. The molecular electron transfer theory based on contributions by Rudolph Marcus (Nobel Prize in Chemistry 1992)[38] so far mainly applied to biopolymers rather than truly conductive polymers, will be briefly explained here. An electron transfer reaction corresponds to motion on a potential energy surface between two minima, corresponding to different stable localizations of an electron. With a naphthalene cation together with an anthracene molecule, the following electron transfer reaction may then take place:

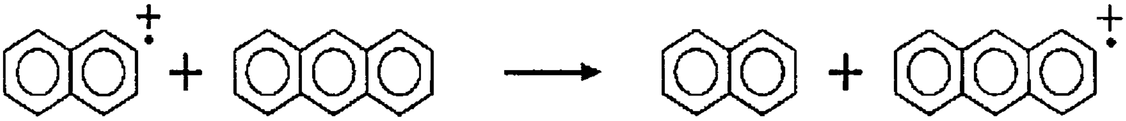


Figure 1.4: Electron transfer reaction

1.4.4 Role of Doping

The role of the dopant is either to remove or to add electrons to the polymer. For example, iodine (I_2) will abstract an electron from the polymer to yield I_3^- ion and the radical cation of the polymer in the oxidative doping process. If an electron is removed from the top of the valence band of a semiconductive polymer, such as polyacetylene or polypyrrole, the vacancy (hole) so created does not delocalise completely, as would be expected from classical band theory. If one imagines that an electron be removed locally from one carbon atom, a radical cation would be obtained. The radical cation (also called a "polaron") is localised, partly because of Coulomb attraction to its counter ion (I_3^-), which has normally a very low mobility, partly because of a local change in the equilibrium geometry of the radical cation relative to the neutral molecule.

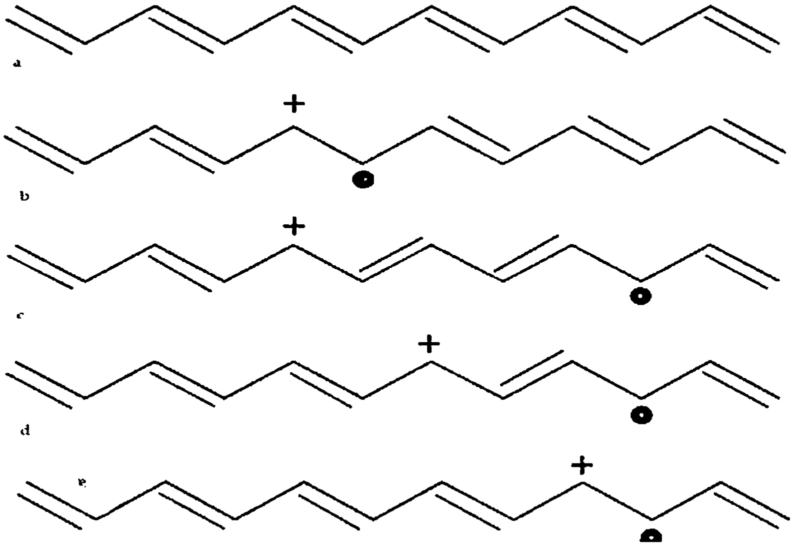


Figure 1.5: Radical cation ("polaron") formed by removal of one electron on the 5th carbon atom of an undecahexaene chain (a → b). The polaron migration shown in c to e.

The mobility of a polaron along the polyacetylene chain can be high and charge is carried along as shown in Figure 1.5. However, since the counter ion to the positive charge is not very mobile, a high concentration of counter ions is required so that the polaron can move in the field of proximal counter ions. This explains why so much doping is necessary. If a second electron is removed from an already-oxidised section of the polymer, either a second independent polaron may be created or, if it is the unpaired electron of the first polaron that is removed, a bipolaron is formed. The two positive charges of the bipolaron are not independent, but move as a pair, like the Cooper pair in the theory of superconductivity. While a polaron, being a radical cation, has a spin of ½, the spins of the bipolarons sum to S = 0. Figure 1.6 shows how a *cis*-polyacetylene chain by undergoing "thermal" isomerisation to *trans* structure may create a defect, a stable free radical: this is a *neutral* soliton which although can propagate along the chain may not itself carry any charge. On the other hand it may contribute to charge transfer between different chains

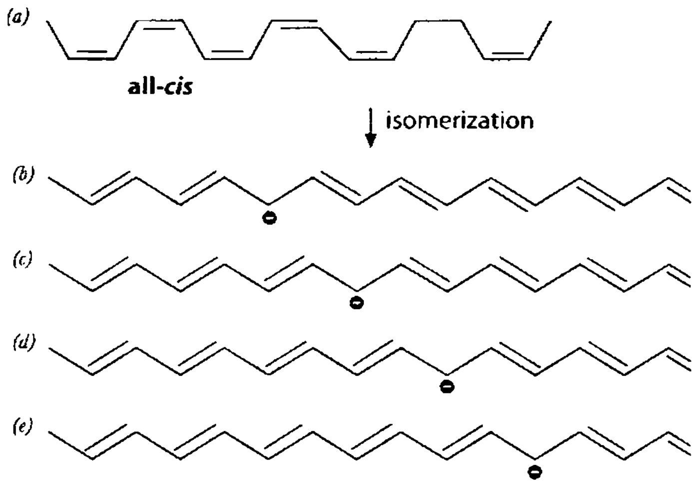


Figure 1.6: A soliton is created by isomerisation of cis polyacetylene (a → b) and moves by pairing to an adjacent electron (b → e).

However, generally solitons made by doping are more important than "bond alternation defects" like the one illustrated in the figure.

Bulk conductivity in the polymer material is limited by the need for the electrons to jump from one chain to the next, *i.e.*, in molecular terms an intermolecular charge transfer reaction. It is also limited by macroscopic factors such as bad contacts between different crystalline domains in the material. One mechanism proposed to account for conductivity by charge hopping between different polymer chains is "intersoliton hopping" (Figure 1.6). Here an electron is jumping between localized states on adjacent polymer chains; the role of the soliton is to move around and to exchange an electron with a closely located charged soliton, which is localised. The mechanism at work in intersoliton hopping is very similar to that operating in most conducting polymers somewhere in between the metallic state at high doping and the semiconducting state at very low doping. All conjugated polymers do not carry solitons, but polarons can be found in most of them. Charge transport in polaron-doped polymers occurs via electron transfer between localized states being formed by charge injection on the chain

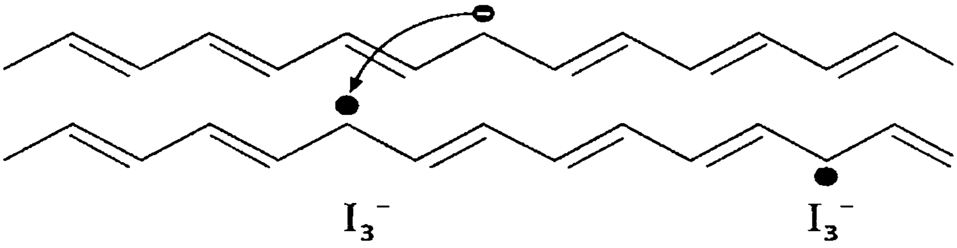


Figure1. 6: Intersoliton hopping: charged solitons (bottom) are trapped by dopant counter ions, while neutral solitons (top) are free to move.

A neutral soliton on a chain close to one with a charged soliton can interact: the electron hops from one defect to the other.

1.5 APPLICATIONS OF CONDUCTING POLYMERS

Though the number of envisioned applications soon mushroomed, attempts to develop industrial scale utilizations of conducting polymers [CPs] have remained limited. This situation essentially resulted from the fact that the present performance of CPs in terms of conductivity, charge storage capacity, and environmental stability are still insufficient to compete with existing technologies. Parallel to this sudden awareness concerning the initially envisioned applications of CPs, the past five years have been marked by an explosion in the number of efforts devoted to new advanced applications.

Molecular electronics (ME) is rapidly evolving from physics, chemistry, biology, electronics and information technology. This is because the present-day advanced silicon chip can store about 16 million bytes of information within an area less than 1 cm^2. Organic materials such as proteins, pigments and conducting polymers (CPs) have been considered as alternatives for carrying out the same functions that are presently being performed by silicon-based semiconductors. Among these, CPs gained the maximum attention. These ME materials differ from conventional polymers by having a delocalized electronic structure that can accommodate charge carriers such as electrons and holes. CPs such as polypyrroles, polythiophenes and polyanilines have been projected for applications for a wide range of ME devices. The major challenge confronting the material scientists including chemists and physicists is unraveling how the properties of these electronic materials differ from those of conventional semiconductors. One of the main reasons for such a widespread interest in CPs is due to their ability to exhibit full range of properties from insulator to superconductor depending upon chemical modification. CPs have applications as optical, electronic, drug-delivery, memory and biosensing devices. Additionally, these materials possess specific advantages such as high packing density and possibility of controlling shape and electronic properties by chemical modification. The very high switching speed and integration density of monocrystalline silicon devices made the development of today's high performance communication systems, personal computers and portable devices possible. CPs that can match these wonderful attributes of monocrytalline silicon is yet to be developed. However, current generation of CPs can rival monocrystalline silicon for several applications. A lot of electronic devices, for example, are still designed to interface the human being with electronic systems. Displays and identification systems like the anti theft chips embedded in modern car keys are typical examples of such applications, which are likely to gain more and more market share in the near future. For this kind of products good mechanical properties, large area coverage and inexpensive manufacturing are much more desirable than high-speed performance or integration density.

There are two main groups of applications for these polymers. The first group utilizes their conductivity as its main property. The second group utilizes their electroactivity. Some of the potential applications of the two groups of CPs are summarized below.

Group 1

Electrostatic materials
Conducting adhesives
Electromagnetic shielding
Printed circuit boards
Artificial nerves
Antistatic clothing

Group 2

Molecular electronics
Electrical displays
Chemical and biochemical sensors
Rechargeable batteries and solid electrolytes
Drug release systems
Optical computers

Thermal sensors
Piezoceramics
Active electronics
Switches
Aircraft structures
Ion exchange membranes
Electromechanical actuators
'Smart' structures

For potential applications in **Molecular Electronics,** a series of functional conjugated oligomers with varying optical and electronic properties have been developed by altering molecular chain length. In molecular electronics, single organic molecules or molecular bundles are employed as building blocks for electronic devices. The most attractive feature of molecular electronics is that organic molecules can be utilized for the fabrication of most of the basic components required in microelectronics such as wires, diodes, transistors, logic gates, memories and switches. π-Conjugated polymers and their oligomer counterparts are some of the most suitable materials for molecular wires, diodes and transistors. These molecules will serve as wires for molecular electronics through self-assembly. Conjugated polymers/oligomers can be functionalised with an "alligator clip" unit at the end of its chains, which allows self-assembly on metal surfaces or metal nanoelectrodes. The potential for low-cost manufacturing using solution processing of film-forming polymers provided further impetus for development and application of these materials in microelectronics. Light displays and integrated circuits, for example, could theoretically be manufactured using simple inkjet printing techniques. The commercialization exemplified by the following list of materials illustrates the impact of Heeger's, McDiarmid's and Shirakawa's work on the later development of conductive polymers.

- Doped polyaniline is used as a conductor and for electromagnetic shielding of electronic circuits. Polyaniline is also employed as a corrosion inhibitor.
- Poly(ethylenedioxythiophene) (PEDOT) doped with polystyrenesulphonic acid is manufactured as an antistatic coating material to prevent electrical discharge exposure on photographic emulsions and also serves as a hole injecting electrode material in polymer light-emitting devices.
- Poly(phenylene vinylidene) derivatives are major candidates for the active layer in pilot production of electroluminescent displays (for example, mobile telephone displays).
- Poly(dialkylfluorene) derivatives are used as the emissive layer in full-colour video matrix displays.
- Poly(thiophene) derivatives are promising for field-effect transistors: They may possibly find a use in supermarket checkouts.
- Poly(pyrrole) has been tested as microwave-absorbing "stealth" (radar-invisible) screen coatings and also as the active thin layer of various sensing devices.

Other possible applications of conductive polymers include supercapacitors and electrolytic-type capacitors. Some conductive polymers such as polyaniline show a whole range of colours as a result of their many protonation and oxidation forms. Their electrochromic properties can be used to produce, e.g. "smart windows" that absorb sunlight in summer. An advantage of polymers over liquid crystals is that they can be fabricated in large sheets and unlimited visual angles. They do not generally respond as fast as in electron-gun displays, because the dopant needs time to migrate into or out from the polymer - but still fast enough for many applications.

Conductive polymers (CPs) experience a volume change when they are subjected to doping. Polyacetylene, polyaniline (PAni), nylon, polypyrrole (PPy) and polythiophene (PT) are examples of conductive polymers. For these to function as conductors, an electrolyte must be present to supply the ions. The application of a small electric field will prompt the electrochemical reactions causing the polymer to become conductive or insulative, thus causing the ions and solvent to migrate either into or out from the polymer matrix resulting in the volume change.

Although carbon nanotubes are not polymers, they are considered to be the most recent addition to this list of electroactive actuators. Carbon nanotubes, known to exhibit sensing and actuating capabilities, are sheets of graphite one atom thick that are rolled into cylinders forming a structure that has a very small diameter (of the order of a nanometer) but a length greater than a micrometer. Applying a voltage to a carbon nanotube structure residing in an electrolyte will cause it to bend achieving strains up to 0.2%.

1.5.1 Electrorheological and Magnetorheological Fluids

Electrorheological (ER) and magnetorheological (MR) fluids experience a nearly instantaneous change in their rheological properties upon the application of an electric or magnetic field, respectively. This change is reversible and occurs also nearly instantaneously upon the removal of the applied field. The physical changes can be quite substantial, turning a low viscosity fluid into a much more viscous, almost-solid substance. These special fluids typically consist of a dispersed, polarizable particulate phase suspended in a carrier fluid. While ER and MR fluids can use the same type of carrier fluid (e.g. high electrical resistivity, low-viscosity substance such as a hydrocarbon or silicone oil), the particulate phase is different. For ER fluids, the dispersed particles are commonly metal oxides, aluminosilicates, silica, organics, or polymers. MR fluids use ferromagnetic or paramagnetic solid particles. Activators, surfactants, and other additives are also commonly included in both types of fluids to improve their properties. ER and MR fluids are mostly considered for damping applications. Specific applications include exercise equipment, valve, braking and clutch systems, as well as in vibration control and shock absorbing systems.

1.5.2 *Electroluminescent and Photoluminescent Materials*

Luminescence is the property of emitting energy in the form of light (having a wavelength in the visible region). The process of luminescence occurs when a material's valence electrons excited to higher energy levels by some stimulus, fall back to lower energy levels giving off photons, or light. Luminescent properties can be classified by the type of input energy used to excite electrons to higher energy levels. In the case of thermoluminescent, electroluminescent and photoluminescent materials, electrons are excited by heat, applied electric field, and incident photons, respectively. Electroluminescence (EL), in basic terms, is the emission of light induced by an applied electric current. Some examples of conjugated (also known as conducting) electroluminescent polymers include poly(alkylfluorenes), polyparaphenylene (PPP), and poly(*p*-pyridine) Other electroluminescent polymers include polythiophenes (PT), poly(phenylene vinylene) (PPV), poly(*p*-phenylene), and polyfluorenes. Polythiophenes and PPVs can exhibit electroluminescence from blue to the near-infrared depending on the side group substituents present in them. Copolymers with an electroactive segment of poly(p-phenylene benzobisthiazole) (PBZT), exhibited photoluminescence with wavelengths representing blue to red visible light. In general, conjugated polyquinolines can be modified to emit light having a wavelength anywhere in the visible spectrum. The most common application of an electroluminescent material is in a light emitting diode/device (LED). LEDs consist of an electroluminescent material sandwiched between two electrodes, one of which is transparent allowing the transmittance of the emitted light.

1.5.3 *Electrochromic Materials*

When an electric current is passed through an electrochromic material its optical properties change such that the material has a significantly different appearance. That is, the absorptive, reflective, or transmissive properties are altered enough to cause a change in its color, reflectivity or transparency. The electrochemical oxidation of polyaniline can change it from being transparent to green, then blue, and then purple. Upon electrochemical reduction this color scheme is reversed, and thus it is an electrochromic material. Polydiphenylamine (PDPA) is another electrochromic polymer. Electrochromic materials can be used to create smart windows capable of reducing their transmittance by at least 65% in less than a minute when an electric field is applied. Once the electric field is removed the effect remains, but it is reversible when the current is reversed.

1.6 CURRENT TRENDS IN CONDUCTING POLYMERS

Conductive polymers opened up new directions in electronics and polymer science. They offer the prospect of materials that combine novel electronic properties with the ease of processing of polymers, and whose properties can be tuned by chemical modification to give desired features. This section is intended to be a comprehensive but by no means exhaustive compilation of the relevant breakthroughs and advances made in the realm of synthesis, morphological changes, conductivity mechanisms and applications in a kaleidoscopic view. A sub section has been devoted to highlight the growing interest in the field of molecular electronics with special emphasis on the field of microwave technology

Conducting polymers including polyaniline are insoluble in common organic solvents, owing to strong inter-chain interactions. Circumventing this problem, a new method for the preparation of conductive polyaniline solutions for application to liquid crystal devices has been achieved by Eli Harlev *et al* employing pyruvic acid to be the solvent/protonating agent such that the dissolution and protonation of emeraldine-base could be carried out simultaneously, yielding true solutions of the conductive emeraldine-salt[39].

Yongsheng Yang and Meixiang Wan have successfully synthesized chiral nanotubes of polyaniline (PAni) by a template-free method in the presence of (*S*)-(2)-2-pyrrolidone-5-carboxylic acid [(*S*)-PCA)] or (*R*)-(1)-2-pyrrolidone-5-carboxylic acid [(*R*)-PCA] as the dopant for the first time. More recently, Wan *et al*[40-45] reported that micro- and nanotubes of PPy and PAni could be synthesized by a template-free method. Chiral conducting polymers are of considerable interest because of their potential applications such as electrodes for electrochemical asymmetric synthesis[46-47], electrodes capable of performing stereoselective analysis[48-49], novel chiral stationary phases for chromatographic separation of enantiomers[50-52], microwave absorbents[53] and electroactive chiral membranes for selective transport of a particular enantiomer[54]. Optically active conducting polymers, such as PPy[55-59], polythiophene (PT)[60-62] and PAni[63-67] have been reported in the literature. AC electrical conductivity of Cr-doped polyaniline/poly(vinyl alcohol) blends have been studied by D.A.W. Soares *et al.* Impedance spectroscopy measurements in the range of 20Hz to 1MHz carried at 100 K and 250 K indicated that thermally activated carrier process between PAni:Cr^{3+} grains in the PAni:Cr^{3+}/PVA blend sample are responsible for its high temperature conductivity[68]. Yuan *et al* have prepared inclusion complexes between polyaniline and β-cyclodextrin from aqueous solution. These encapsulated polymers with high potential application help to understand the mechanism of conduction and applications in molecular electronics as nanowires[69]. Similar work focused on the polymerization of aniline in the cavity of clay and zeolites have been carried out by Wu *et al* and Enzel *et al.* Ita *et al* carried out detailed investigations on polyaniline/silica hybrid gels that were prepared by chemical polymerization of aniline in the sol-gel systems of tetramethoxysilane using ammonium peroxydisulphate as initiator and sodium dodecyl sulphate as stabilizer. The emeraldine salt polyaniline was dispersed uniformly in sol-gel silica by polymerising aniline during the wet gel stage[70].

Ghosh has carried out a theoretical correlation of the near-neighbour interactions in protonation of polyaniline[71]. It would be interesting to apply the concept of nearest-neighbour interactions to the process of doping of other conducting polymers where strong nearest-neighbour interaction may lead to the appearance of two redox potentials for the same redox process.

Cruz-Estrada and M. J. Folkes published a two part write up concerned with structure formation and modeling of the electrical conductivity in a polyaniline filled composite following an approach based on percolation theory and secondly on a correlation found between the composite's morphology and its conductivity behaviour[72].

A study on Hall voltage and electrical resistivity of doped conducting polyaniline was done by Ghosh *et al*[73]. The resistivity of the sample has been observed to show a decreasing trend with increase in temperature. From the conductivity versus temperature plot, different physical quantities such as localisation length and molecular vibrational frequency have been determined.

Cao *et al*[74] studied the influence of chemical polymerization conditions on the properties of polyaniline by various oxidizing agents. Yasuda and Shimidzu[75] synthesized polyaniline using $FeCl_3$ as oxidant, but the yield and conductivity of the polymer produced were very low. Polyaniline was obtained in 60% yield with a conductivity of 10 Scm^{-1} using H_2O_2-Fe^{2+} system by Sun *et al*[76]. An optimization study on polyaniline prepared via potassium iodate oxidation route was carried out by Armes and Aldissi[77]. Palaniappan *et al* examined the effects of benzoyl peroxide as oxidizing agent, different protonic acids, aniline/oxidizing agent ratio, temperature and time, etc. on polymer properties, with special emphasis on the yield and conductivity of polyaniline. Apart from being conducting polymers, polyaniline and its salts have also found application as catalysts for a variety of transformations: polyaniline salt, for example, was used as catalyst for the esterification reaction of phenyl acetic acid with methanol. Reports by Palaniappan *et al* reveals the use of polyaniline salts and polyaniline complexes as catalyst for the first time in bisindole synthesis. Bisindole (3,3,0-bis(indolyl)phenylmethane) is obtained in excellent yields in a simple and more environmentally benign procedure[78]. The use of polyaniline catalysts are feasible because of their easy preparation, easy handling, stability, easy recovery, reusability, good activity and eco-friendly nature. Palaniappan *et al* have also developed processes for the preparation of polyaniline salts such as polyaniline-sulphate, polyaniline-nitrate and polyaniline-hydrochloride by emulsion polymerization pathway. This was achieved by oxidizing aniline to the corresponding polyaniline salt using benzoyl peroxide as an oxidizing agent in the presence of sulphuric, nitric, or hydrochloric acid by emulsion polymerization pathway. Polyaniline salts and their corresponding bases were characterized by infrared, electronic absorption and X-ray photoelectron spectral techniques, scanning electron microscopy, X-ray diffraction, elemental analysis, and conductivity measurements. The results of this study indicated that both acid and surfactant groups are present in the polyaniline salt as dopants[79]. Pron *et al*[80] have compared the use of four different oxidizing agents $(NH_4)_2S_2O_8$, $K_2Cr_2O_7$, H_2O_2 and KIO_3 in the polymerization of aniline.

Tsotcheva *et al*[81] carried out structural studies of powdered polyaniline (PAni) prepared in aqueous medium by the oxidative polymerization of aniline in the presence of dodecylbenzenesulfonic acid (DBSA) employing DSC and WAXS. It was found that DBSA induces crystallinity in the rigid matrix of PAni, and residual crystalline phases were also observed after the deprotonation of PAni-DBSA. For the first time, a melting peak and a relaxation transition of non-cross-linked PAni were registered. Pomposo *et al* [82] have synthesized polyaniline in the presence of a mixture of hydrochloric acid and formic acid and ammonium persulphate as oxidant. The polymer, with a conductivity of 25-30 Scm^{-1}, obtained thereby is used to formulate conducting paints. A stable paint with a conductivity of 10^{-3} Scm^{-1}is obtained.

Thermal transporting properties of electrically conductive polyaniline films as organic thermoelectric materials was investigated recently by Toshima *et al*[83]. Thermogravimetric study of PVC-PAn blends by R. F. de Farias and L. M. Nunes[84] suggested that the thermal stability of the synthesized blend is decreased as the total amount of PAni is enhanced. Furthermore, the Brönsted acid doped blend is more stable than the corresponding undoped one. PVC and the PVC-PAni blends exhibit two mass loss steps.

H. Zheng[85] suggested a plausible pathway for the construction of a polyphenol oxidase-based biosensor from an *in situ* electropolymerized polyaniline-polyacrylonitrile composite film. The PAni composite particles exhibit many advantages as a controllable polarization body in the ER fluid system since it is possible to tailor particle characteristics including the composition ratio, the particle conductivity, and the particle size[86]. Electrorheological properties of a polyaniline-montmorillonite clay nanocomposite suspension investigated by Jun Lu and G Zhao showed that this anhydrous PAni-MMT ER fluid not only displayed notable ER properties under DC electric field over a wide temperature range but also possess excellent anti-sedimentation stability under a DC electric field[87]. M. S. Cho, Lee Choi studied a dry-base electrorheological (ER) fluid which was prepared by dispersing synthesized semiconducting polyaniline (PAni) particles into silicone oil, and its viscoelastic properties were investigated under applied electric fields using a rotational rheometer. Within the linear viscoelastic region, the ER fluid was observed to be elastic due to columnar structure of PAni particles sustaining the deformation[88]. Jhon *et al* microencapsulated homopolyaniline particles with melamine-formaldehyde resin and then investigated their ER characteristics[89]. Microencapsulation entraps core liquid materials by circulating them with certain polymeric materials. Upon application of an electric field, the suspended dielectric particles in an ER fluid align themselves into chains and columns parallel to the field, thereby inducing yield phenomenon, viscoelasticity, and a drastic increase in viscosity. Because of their controllable viscosity and fast response, ER fluids are regarded as a smart material for active devices, which can transform electric energy to mechanical energy. Ohad, Levyy and Stroudz have studied the macroscopic disorder and the metal-insulator transition in conducting polymers and suggested a model for treating the frequency-dependent conductivity and dielectric function for a quasi-one-dimensional conducting polymer[90]. Narula *et al* have studied the A.C. conductivity and dielectric constant of poly(*N*-methylpyrrole) thin films in the temperature range 77-350 K and in the frequency range 10^2–10^6 Hz. The well-defined loss peaks have been observed in the temperature region where measured AC conductivity approaches D.C. conductivity. These loss peaks are associated with the hopping of the charge carriers. The frequency and temperature dependence of A.C. conductivity have been qualitatively explained by considering the contribution from two mechanisms; one giving a linear dependence of conductivity on frequency and other having distribution of relaxation times giving rise to broad dielectric loss peak[91].

The dielectric and conductivity relaxations in other conducting polymers have been discussed and analyzed in light of the model of multiple conductivity relaxation modes[92]. Wessling *et al* carried out measurements on the low-temperature heat capacities of polyaniline and polyaniline-polymethylmethacrylate blends using the free-electron model, the corresponding density of states at the Fermi level were calculated and compared with those obtained from magnetic susceptibility measurements on the same samples[93]. High dielectric constant polymer composite materials are being developed by the electronic industry in response to the need for power-ground decoupling to secure integrity of high speed signals and reduce electromagnetic interference (EMI) radiated noise. High dielectric constant values ranging between ca. 200-1000 have been reported recently for a PAni/PVA (Polyvinyl alcohol) composite[94]. This report gave no structural analysis results for the composite, but just stated that the dispersing submicronic PAni particles are suspended in the insulating matrix PVA. Some novel nanostructure composites made of epoxy and lead magnesium niobate-lead titanate were reported to have very high dielectric constant[95]. A similar epoxy-based composite with an ultra high dielectric constant (~1000) has been developed by Y. Rao and C.P. Wong[96]. Nevertheless, some studies did indicate that PAni and some PAni/polymer blends are capable of exhibiting a high dielectric constant. For instance, a dielectric constant of $\geq 10^4$ can be observed in a partially crystalline PAni sample system developed by MacDiarmid *et al*. An inhomogeneous disorder model was proposed for this system, in which ordered (crystalline) region, described by three-dimensional metallic states, is connected through amorphous region of polymer chains where one-dimensional disorder-induced localization is dominant[97].

A novel microwave method for measuring the complex dielectric constant of polymer thin sheets has been suggested by Bhoopathy and Anandavadivel[98]. This method is used to measure the complex dielectric constant of poly(ethylene vinyl acetate), polyurethane, polyvinyl acetate, and polystyrene. The results obtained are in good agreement with literature. This technique provides adequate interaction of microwaves with the sample effectively. In order to measure complex dielectric constant of polymers, the thin sheets of samples were prepared by the method of solution evaporation[99] to avoid the change of properties due to heating[100]. The prepared samples were kept at a transverse plane in wave-guide section for TE10 mode. Rezende *et al* have carried out radar cross-section measurements (8-12 GHz) of magnetic and dielectric microwave absorbing thin sheets. Magnetic MnZn, NiZn, MgZn ferrites and iron carbonyl in an elastomeric matrix (urethane or silicone rubber), in the form of thin flexible sheets and dielectric: conducting polymer - based on polyaniline (PAni), in a elastomeric matrix (EPDM - ethylene propylene diene terpolymer), in the form of thin flexible sheets were employed in the study[101].

In the investigation carried out by Sengwa *et al*, an attempt was made to evaluate the microwave dielectric relaxation times of 5, 10, 20 and 30 wt% PVP concentrations in PVP-PEG mixtures in dilute solutions in benzene at 10.1GHz and 35°C[102]. In this work, the elongation behaviour of the intermolecular structure of heterogeneous polymeric networks and their intramolecular rotations in dilute solution have been explored in order to determine their molecular conformations. It is also interesting to study the relaxation behaviour at 10.1GHz because the dielectric loss peak of the polymers in dilute solutions of nonpolar solvents occurs around 10 GHz. The relaxation times of these mixtures are independent of their viscosity, but the elongation of the mixture network is influenced by the PEG chain length and the number of hydroxyl groups in comparison with the number of carbonyl groups in the mixtures. Dielectric relaxation studies of poly(propylene glycol), average molecular weight 2000 gmol^{-1}, in dilute solution of cyclohexane, decaline, benzene and carbon tetrachloride have been carried out at 10 GHz and 35 °C[103].

Measurements of dielectric parameters as a function of frequency and temperature are among the well-established methods for detecting dipole reorientation by molecular and group rotations. Baur and Stockmayer[104] carried out the first systematic dielectric dispersion study of pure poly(propylene glycols) of different molecular weight in the glass transition (T_g) region and found that the principal dispersion occurs at the same frequency for all molecular weights at a given temperature, but at lower frequencies there is a small secondary loss peak which depends strongly on molecular weight. Later, dielectric properties of pure PPG were thoroughly studied by several workers[105-108]. These dielectric studies confirmed a β relaxation process below the glass transition temperature, T_g (about 200 K). This relaxation process is attributed to the cooperative motion of several repeat units of the chain accompanying the methyl group reorientation. Above Tg, there are two additional relaxation processes in PPG molecules[108]. The principal one is the α relaxation with which the β relaxation merges at about 250 K. Beevers *et al*[109] measured the dielectric relaxation times and electro-optical Kerr-effect relaxation times for melt samples of pure PPG (MW 1025, 2025 and 4000 gmol^{-1}) and also confirmed that there are two relaxation processes in the temperature range 209±255K. Recently, Schonhal and Stauga[110] studied the molecular dynamics of PPG liquids (MW 1200, 2000 and 4000 gmol^{-1}) confined to porous glasses using dielectric spectroscopy. Beside the α relaxation, they also found relaxation at lower frequencies which was strongly pore-size-dependent and was assigned to the dynamics of the whole chain or a longer part of it. Similarly, Carini *et al*[111] have also studied the reorientational relaxation dynamics of H-bonded neat liquid propylene glycol molecules confined in porous silica gels by Rayleigh wing spectroscopy, and the effect of hydrogen bonding on relaxation dynamics was clearly demonstrated. Further, Kimura *et al*[112] have shown that the phase structure and physical properties of urethane modified poly(propylene glycol)/poly(dimethylsiloxane) blend can be controlled using an electric field.

Mariz and Neto carried out complex conductance measurements of polyaniline/carnauba wax composites at room temperature in samples containing different amounts of PAni as a function of the frequency[113].

1.6.1 Microtubules and microemulsions

Recently considerable attention has been directed towards hollow tubular structures. Hollow nanotubes have novel properties and possess different contact areas that can be functionalized in various ways. Conducting polymer nanotubes have been synthesized to tap their potential applications[114] as nano-sized transistors, displays, and sensors. In addition, nanotubes and nanofibers of conducting polymers are excellent candidates for application as molecular wire materials because of their one-dimensional structures and metal-like conductivity. Martin *et al*[115] fabricated conducting polymer nanotubes and nanofibers by filling the nanopores of anodic aluminium oxide (AAO) or organic polymer filters. They reported that tubular and fibrillar nanostructures of conducting polymers have the potential to display a much higher conductivity than the bulk forms. Thus, polypyrrole, polythiophene and poly(*p*-phenylene vinylene) nanotubes[116] have been synthesized. Most of these investigations have been focused on synthetic methods using organic/inorganic templates like alumina and polycarbonate membranes.

Wan *et a*[117] have reported the preparation of polyaniline tubular nanostructures through self-assembly in the presence of a dopant, which acted as a template. Especially, PPy tubular structures[118] prepared by the self-assembly method have only been achieved with micrometer-sized diameters and low aspect ratios. Polypyrrole (PPy) nanotubes have been fabricated by reverse microemulsion polymerization in a nonpolar solvent. Factors affecting the formation of PPy nanotubes have also been investigated by Jang and Yoon[119].

Tamilselvan *et al*[120] studied the generation of polyaniline microstructures employing four different microemulsion systems using anionic surfactants. The synthesis of microtubules or molecular wires of conducting polymers is undoubtedly attractive and significant. A method termed *template synthesis*[121] has been used to obtain microtubules of conducting polymers. This method is an effective way of synthesizing microtubules of conducting polymers, and it has been applied to the synthesis of microtubules of polyacetylene[122], polypyrrole[122,123], 3,4 poly(3-methylthiophene)[124], polyaniline (PAni)[125,126] and even metallic materials[127,128]. Obviously, the template synthesis method has the advantage of controlling the length and diameter of the polymer microtubules by using the right templates. Recently, Huang and Wan[129] found that conducting microtubules of PAni could be synthesized by *in situ* doping polymerization (ISDP) in the presence of п-naphthalenesulfonic acid (NSA) as the dopant but in the absence of a template. Microtubules of polyaniline doped with HCl and HBF_4 and β-naphthalenesulfonic acid (NSA) have been prepared by Wan and Li. In a recent publication by the same group these microtubules prepared in the presence of a chiral enitity like glucose have been employed as a microwave absorbent material[130]. Wang and Wan accomplished the direct observation of conformational transitions for polyaniline chains intercalated in clay particles upon secondary doping[131]. Their findings constitute the first observation of a significant increase in the inter-sheet distance (i.e. gallery height) of the polymer intercalated clay particles upon the secondary doping, attributable to the conformational transition of the polymer chains from a "compact coil" to an "expanded coil".

Xia and Wang synthesized conductive polyaniline nanoparticles through ultrasonic assisted inverse microemulsion pathway in which the polymerization of aniline was confined to a nanoreactor named 'water pool' surrounded by surfactant molecules in the nonpolar continuous phase. The size of the PAni nanoparticles decreased with the decrease of the *w* value. The spherical nanoparticles (10-50 nm) can further form the uniform submicrometer aggregates with a size of 200-400 nm induced by ethanol. The morphology of aggregates as well as aggregation behavior of PAni nanoparticles was characterized by TEM. The polymerization rate, UV-vis absorption spectra, FTIR spectra, XRD, as well as the conductivity were examined at different [water]/[surfactant] molar ratios, i.e. *w* value. Microemulsions have been extensively used for synthesis of metallic[132], semiconductive[133], polymeric nanoparticles[134,135,136,137]. The technique is useful for large-scale production of nanoparticles using relatively simple and inexpensive hardware. Gan[138] and Selvan[139] reported the microemulsion preparation of PAni nanoparticles by employing sodium bis(2-ethylhexyl)sulfosuccinate (AOT)-water-cyclohexane microemulsion system, however, the polymerization rate is slow and the morphology of PAni is irregular and not uniform. So, preparation of PAni nanoparticles with a uniform size and regular shape requires new methods and new technology. Wang *et al* reported that aggregates of nano silica can be broken apart and be redispersed in the aqueous medium, and thus the long-term stable polymer/nano silica composite latex can be prepared through ultrasonic irradiation[140,141].

1.6.2 *Dielectric Science and Technology*

Dielectric science has enjoyed a long and illustrious history. Dielectric materials have been used in numerous applications encompassing coatings on conductors (e.g., cables, wires), passive devices in circuits (e.g., capacitors), insulators in active devices (e.g., gates, dielectrics in transistors), and isolation between devices in integrated circuits. In addition, dielectric science has been a longstanding branch of physics with close links to chemistry and electrical engineering. It is generally accepted that a dielectric material interacts with an electric field differently than does free space because the dielectric contains charges that can be displaced. Because all materials contain charges, essentially every material can be classified as a dielectric.

Dielectric studies involve measurements of permittivity and dielectric loss. The measurements can be used to find dielectric relaxation times and distribution parameters. The relaxation time depends on the molecular size, shape, intramolecular and intermolecular forces, and can be used to investigate molecular and intramolecular motions and their relation to molecular structure. These studies can be used to evaluate the barrier height hindering internal rotation, problems of complex formation, dipole-dipole interactions and other short-range intermolecular forces. Although NMR, ESR and IR spectroscopy are powerful tools for studying hydrogen bonding, dielectric relaxation measurements have great potential for studying weak molecular interactions. An extensive study of dielectric behaviour of polar solutes at low concentration (to minimize solute-solute interactions) in non-polar solvents has led to valuable information regarding hydrogen bonding and solute-solvent interactions. Intrinsically, conducting polymers such as polyaniline exhibit unusually high polarizability and high dielectric constant, which extends into microwave range. Typically, the frequency dependent dielectric permittivity in organic polymers is dominated by reorientation of molecular dipoles[142]. Since at higher frequencies the orientational polarization vanishes and the polarizability is determined by the localized electronic states, the relative dielectric permittivity of most organic polymers drops to a low value of about 2-3 approaching a square of the refractive index at optical frequencies. Several investigations of polyaniline salts indicate that its microwave dielectric constant is considerably higher than that of organic solids. It has been reported that the dielectric constant of cross-linked emeraldine salts is proportional to the square of the crystalline domain coherence length and increases from about 800 to about 3.3×10^4 with increasing crystallinity of the macroscopic metallic domains[143]. Investigations by Youngs[144], indicated that the dielectric constant of polyaniline protonated with HCl decreases from about 1×10^7 at 100 Hz to about 1×10^2 at 1 GHz. Naishadham *et al* measured the permittivity of protonated polyaniline between 2 GHz and 18 GHz in a coaxial line. Their results indicated real permittivity of about 100 at 2 GHz, which decreased to below 2 at12 GHz[145]. Many of the discrepancies in reported permittivity of conducting polyaniline, especially at microwave frequencies, seem to be a result of variation in composition and application of non-standard measurement protocol. Obrzut and Chiang[146] has studied the electromagnetic properties, permittivity and conductivity of emeraldine salt and its epoxy resin composites in the microwave frequency range. The observed high value of the microwave dielectric constant is attributed to polarizability originating from a delayed charge transfer between conducting domains with an apparent relaxation at about 6.8 GHz. In composites in which coupling between the conducting domains is weakened by a non-conducting phase boundary, the microwave dielectric polarizability becomes reminiscent of localized states in organic solids. Development of the composite materials for high frequency applications requires thorough understanding of the materials behavior at the frequencies of interest. Walpita *et al*, Jones *et al* and Truong *et al* have investigated ferroelectric ceramic/polymer composites at the frequencies above 1 MHz[147,148-150]. To-date, no systematic study on the dielectric properties of ferroelectric ceramic/polymer composites over a broad frequency range that would include microwave frequencies has been reported. Recently, Obrzut *et al* have developed a new measurement technique for solid films, which facilitated dielectric study of materials at high frequencies[151]. Based on the same technique, Popielarz *et al* carried out an elaborate study of the temperature and frequency dependence on dielectric properties of polymer/ferroelectric ceramic composites from 100 Hz to 10 GHz. The study has also shed light on the effect of different polymer matrices on dielectric properties of the composites, the relationship between the dielectric constant and the composite composition and thermal sensitivity of the dielectric response[152].

1.7 HIGH FREQUENCIES, MICROWAVES AND MATTER

The microwave radiations constitutes only a small portion of electromagnetic spectrum (300 MHz to 300 GHz) but their uses have become increasingly important in the modern world. The dielectric parameters over a wide range of temperature on low loss dielectrics are needed to assess their suitability for use in telecommunications, dielectric waveguides, lenses, radomes, dielectric resonators and microwave integrated circuit (MIC) substrates and on lossy materials for estimating their heating response in microwave heating applications. The dielectric data would also be required on lossy ceramics for their use as microwave absorbers lossy pastes for the design of new food packages, heating in microwave ovens and biological materials for diathermy. The ISM band of frequencies (2-4 GHz) is of great utility in Industrial, Scientific and Medical (ISM) applications. Microwave heating is a very efficient method of heating dielectric materials and is extensively used in industrial as well as household heating applications. Microwaves only partially reflect from and freely propagate through dielectric materials (i.e. ceramics). It is the combination of these two conditions, which allowed the development of a reflection method that permits the measurement of dielectric properties and physical dimensions.

1.7.1 Polarization

The interaction of microwaves with dielectric materials causes a net polarization of the substance. There are several mechanisms, which are responsible for this occurrence, including: electronic, ionic, molecular (dipole), and interfacial (space-charge) polarization. In general, the addition of an applied field in a normal state will cause a displacement of charge, which results in a polarization in the direction of the field. For a given material, the sum of the contributions from each mechanism determines the net polarization, P, of the dielectric material.

P= Pelectronic+ Pionic+ Pmolecular+ Pinterfacial

Electronic Polarization

For a dielectric material in a normal state, electrons are bound to their parent atoms and are fixed to their equilibrium positions. This mechanism becomes apparent upon application of an electric field, under which the electrons are shifted from equilibrium with respect to the positive nuclei in the direction of the field. In this state the atom acts as a temporary induced dipole.

Ionic or Atomic Polarization

Ionic or atomic polarization differs from the electronic mechanism in that it occurs due to the relative motion of the atoms instead of a shift of the electron clouds surrounding atoms. Under an applied field, a separation of charge is caused which yields a displacement of the cations and anions in crystals relative to their equilibrium positions. Specifically, cations are attracted toward the negative electrode and anions are attracted toward the positive electrode.

Molecular Polarization

Molecules are randomly oriented in a material in a normal state so that there is no net charge present. Molecular or dipole polarization occurs when an external field aligns permanent dipoles parallel to the field. In some materials this polarization can be retained upon removal of the field due to the need for thermal activation of molecular rotation. These electrostrictive or piezoelectric materials are called electrets and are the electric field analogs of magnets.

Interfacial Polarization

In interfacial or space-charge polarization, mobile charge carriers in a heterogeneous material are accelerated by an applied field until they are impeded by and pile up at physical barriers. This build up of charge dictates the polarization of the material. Grain/ phase boundaries and free surfaces are common barriers. The polarization resulting from the mechanisms above is strongly influenced by frequency. The individual mechanisms have varied dependences of their polarization upon frequencies. In general the larger the masses involved, the slower the response upon application or removal of a field and consequently the relaxation frequency is lower. For example, electronic and ionic polarization mechanisms undergo resonance in the optical and far infrared wavelengths respectively.

1.8 SCOPE AND OBJECTIVES OF THE PRESENT WORK

Most of the conventional conducting polymers, being intractable and infusible, their applications are not fully exploited. The main objective of the proposed study is to develop novel polyaniline based conducting polymers for specific use in the high frequency [0.05-13 MHz] and ISM band frequency of 2-4 GHz. For generating and utilising novel polyaniline based conducting polymers the following broad methodology is proposed.

1. Exploitation of new synthetic pathways using microemulsion technique
2. Use of organic dopants and chiral sugars and the investigations of the resulting morphology changes
3. Developing a composite material based on polyaniline for improving processability.

The specific objectives of the work are

1. Optimisation of synthesis conditions and dopants for improving the the dielectric properties of polyaniline, poly(*o*-toluidine), poly(*o*-anisidine) in the high frequency [1kHz-13 MHz] and microwave frequency of 2- 4 GHz.
2. Use of organic dopants and co-dopants on the particle dimensions and morphology of polyaniline and poly (o-toluidine).
3. Preparation and characterisation of microemulsions of polyaniline as a new route to obtain a uniform morphology and examining its effect on dielectric behaviour.
4. Preparation and characterization of composites of polyaniline and its analogues with polyvinylchloride and different forms of silica and evaluation of their dielectric properties in the microwave frequencies.

5. Comparison of the dielectric properties of polyaniline and it analogues.
6. Investigations of the possible applications of the novel materials developed.

1.9 REFERENCES

1. Wirth, H. O.; Herrman, F. U.; Kern, W. Macromol. Chem. 1964,80, 120.
2. Rothe, M. In Chemistry and Physics of Macromolecules; Fischer, E. W., Schulz, R. C., Sillescu, H., Eds.; VCH: Weinheim, 1991; p 39.
3. Tour, J. M. Trends Polym. Sci. 1994, 2, 332.
4. Shirakawa, H. ; Louis, E.J. ; MacDiarmid, A.G.; . Chiang C.K and. Heeger, A.J. J Chem Soc Chem Comm. 1977, 579.
5. Ito, T ; Shirakawa, H and Ikeda, S. J.Polym.Sci.,Polym.Chem. Ed. 12,1974, 11.
6. Chiang, C.K ;. Fischer, C.R ; Park, Y.W ; Heeger, A.J ; Shirakawa, H. ; Louis, E.J ; Gau, S.C and MacDiarmid, A.G. Phys. Rev. Letters 39 (1977) 1098
7. Chiang, C.K.; Druy, M.A.; Gau, S.C; Heeger, A.J; Louis, E.J; MacDiarmid*, A.G; Park, Y.W and Shirakawa, H. J. Am. Chem. Soc. 100 (1978) 1013
8. Feast, W.J., Tsibouklis, J., Pouwer, K.L., Gronendaal, L. and Meijer, E.W. Polymer 1996,37,5017.
9. Kanatzidis, M.G. Chem. Eng. News 1990,3, 36.
10. Roth, S. "One-Dimensional Metals" Weinheim VCH, 1995.
11. Salaneck, W. R; Lundström, I. and Rånby, B. Ed's (Oxford Sci., Oxford, 1993) Nobel Symposium in Chemistry: Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure,

12. Patil, A. O.; Heeger, A. J.; Wudl, F. Chem. Rev. 1988, 88, 183.

13. Ito, T.; Shirakawa, H. Ikeda, S. J. Polym. Sci. Chem. Ed. 1974,12, 11.

14. Chiang, C. K.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis,E. J.; MacDiarmid, A. G. Phys. Rev. Lett. 1977, 39, 1098.

15. Diaz, A. F.; Kanazawa, K. K.; Gardini, G. P. J. Chem. Soc., Chem. Commun. 1979, 635.

16. Diaz, A. F.; Lacroix, J. C. New J. Chem. 1988, 12, 171.

17. Kovacic, P.; Jones, M. B. Chem. Rev. 1987, 87, 357.

18. Genies, E. M. New J. Chem. 1989.

19. Diaz, A. F. Chem. Scr. 1981, 17, 142.

20. Roncali, J. Chem. Rev. 1992, 92, 711.

21. Mertz, A. Topics in Current Chemistry; Springer-Verlag: Berlin,1990; Vol. 152, p 49.

22. Deronzier, A.; Moutet, J. C. Acc. Chem. Res. 1989, 22, 249.

23. Burroughes, J. H; Bradley, D. C. C; Brown, A. R; Mackay, M. K; Friend, R. H; Burn, P. L. Nature 1990, 347, 539. Greenham, N. C; Friend, R. H; Solid State Phys. 1995, 49, 1. Kraft, A; Grimsdale, A. C; Holmes, A. B; Angew. Chem. Int. Ed. 1998, 37, 402.
    Friend, R. H; Gymer, R. W; Holmes, A. B; Burroughes, J. H; Marks, R. N; Taliani, C; Bradley, D. D. C; Dos Santos, D. A; Brÿdas, J. L; Lˆgdlund, M; Salaneck, W. R. Nature 1999, 397, 121.

24. Hide, F; Dìaz-Garcìa, M. A; Schwartz, B. J; Heeger, A. J. Acc. Chem. Res.1997, 30, 430

25. Wessling, R. A. J. Polym. Sci., Part C: Polym. Symp. 1985, 72, 55.

26. Thakur, M. Macromolecules 1988, 21, 661.

27. Nature 1988, 333, 296. New Sci. 1988, July 28, 39. Sci.Am. 1988, August 12. Chem. Eng. News 1990, May 7, 53.

28. Dai, L; White, J. W. Polymer 1991, 32, 2120.
    Dai, L. J. Phys. Chem. 1992, 96, 6469.
    Dai, L; Mau, A. W. H; Griesser, H. J; Winkler, D. A. Macromolecules 1994, 27, 6728.

29. Bates, F. S;Baker, G. L. Macromolecules 1983, 16, 704.
    Bates, F. S;Baker, G. L.Macromolecules 1984, 17, 2619.

30. Aldissi, M. Synth. Met. 1986, 13, 87.

31. Galvin, M. E; Wnek, G. E.Polym. Bull. 1985, 13, 109. Armes, S; Vincent, B; White, J. W.J. Chem. Soc., Chem. Commun. 1986, 1525.

32. Dai, L; White, J. W in Polymers and Organic Solids (Eds: L. Shi, D. Zhu), Science Press, Beijing 1997, pp. 287±321.
    Dai, L. Macromol. Chem. Phys. 1997, 189, 1723.

33. Luttinger, L. B. J. Org. Chem. 1962, 27, 1591.

34. Hawker, C. J. Adv. Polym. Sci. 1999, 147, 113.

35. Voit, B. J. Polym. Sci., Part A: Polym. Chem. 2000, 38, 2505.

36. Frÿchet, J. M. J; Hawker, C. J. J. Macromol. Sci., Pure Appl. Chem. A 1996, 33, 1399.

37. Wu, I.-Y; Lin, J. T; Tao, Y.-T; Balasubramaniam, E. Adv. Mater. 2000, 12, 668.

Hullim, M; Pillow, N. G; Samuel, I. D. W. Adv. Mater. 1999, 11, 371.
Tao, X. T; Zhang, Y. D; Wada, T. Adv. Mater. 1998, 10, 226.

38. Marcus, R.A. J. Chem. Phys. 1956, 36, 966 Annual Rev. Phys. Chem 15 (1964) 155

39. Harlev, E; Gulakhmedova, T; Rubinovich, I and Aizenshtein, G. Adv. Mater, 1996, 8, No. 12

40. Yang, Y and Wan M. J. Mater. Chem., 2002, 12, 897

41. Wan, M; Shen, Y and Huang, J. Chinese Patent No. 981099165, 1998.

42. Huang, J and Wan, M. J. Polym. Sci. Part A: Polym. Chem., 1999, 37, 1277.

43. Shen, Y and Wan, M. J. Polym. Sci. Part A: Polym. Chem., 1999, 37, 1443.

44. Wan, M and. Li, J J. Polym. Sci. Part A: Polym. Chem., 1999, 37, 4605.

45. (a) Wan, M; Huang, J and Shen, Y. Synth. Met., 1999, 101, 708;

(b) Qiu, H.;Wan, M; Matthews, B and Dai, L. Macromolecules, 2001, 34, 675.

46. MSchwientek, Plens, S and Hamann, C. H. J. Electroanal. Chem., 1999, 461, 94.

47. Pleus, S and Schwientek, M. Synth. Met., 1998, 95, 233.
20 Chen, Z. D; Takei, Y; DeoYe, B. A.and Nagaoka, T.Analyst, 2000, 125, 2249.

48. (a) Mare, L; Diadier, D; Robert, G; Alain, G and Jean, R. J. Chem. Soc., Chem. Commun., 1988, 658;

    (b) Zhou, Y. X; Yu, B and Zhu, G. Y. Polymer, 1997, 38, 5493.

49. Lee, H. S and Hong, J. J. Chromatogr. A., 2000, 868, 189.

50. Chen, Z. D; Okimoto, A; Kiyonaga, T. and Nagaoka, T. Anal.Chem., 1999, 71, 1834.

51. Guo, H. L; Nobler, C. M; and Kaner, R. B. Synth. Met., 1999, 101, 44.

52. Sun, G. C; Yao, K. L; Liao, H. X; Niu, Z. C and Liu, Z. L. Int. J. Electron., 2000, 87, 735.

53. Kane-Maguire, L. A. P; Norris, I. D and Wallace, G. G Synth.Met., 1999, 101, 817.

54. Delabouglise, D and Garnier, F. Synth. Met., 1990, 39, 117.

55. Salmon, M; Saloma, M; Bidan, G and Genies, E. M. Electrochim. Acta, 1989, 34, 117.

56. Moutet, J. C; Saint-Aman, E; Tran-Van, F; Angibeaud, P and Utille, J. P. Adv. Mater., 1992, 4, 511.

57. (a) Elsenbaumer, R. L;Eckhardt, H; Iqbal, Z; Toth, J. and Baughman, R. H. Mol. Cryst. Liq. Cryst., 1988, 917; (b) Chen, F; Akhtar, P; Kane-Maguire, L. A. P.and Wallace, G. G. Aust. J. Chem., 1997, 50, 939.

58. Kotkar, D; Joshi, V and Ghosh, P. K. J. Chem. Soc., Chem.Commun., 1988, 917.

59. (a) Lemaire, M; Delabouglise, D; Garreau, R; Gay, A and Roncali, J. J. Chem. Soc., Chem. Commun., 1988, 658.

60. (b) Lemaire, M; Delabouglise, D; Garreau, R. and Roncal, J. Chim. Phys.-Chim. Biol., 1989, 86, 193.

61. Anderson, M; Ekeblad, P. O; Hjertberg, T; Wennestro¨m, O. and Ingana¨s, O. Polymer, 1991, 32, 546.

62. Asharf, S. A; Kane-Maguire, L. A. P; Majidi, M. R; Pyne S. G and Wallace, G. G. Polymer, 1997, 38, 2627.

63. Majidi, M. R; Kane-Maguire, L. A. P and Wallace, G. G. Aust. J. Chem., 1998, 51, 23.

64. Strounina, E. V L. A. P. Kane-Maguire and G. G. Wallace, Synth.Met., 1999, 106, 129.

65. 37 Norris, I. D; Kane-Maguire, L. A. P; Wallace, G. G and Mattoso, L. H. C. Aust. J. Chem., 2000, 153, 89.

66. Barris, J. V; Innis, P. C; Kane-Maguire, L. A. P; Norris, I. D and Wallace, G. G. Synth. Met., 1997, 84, 181.

67. Majidi, M. R; Kane-Maguire, L. A. P and Wallace, G. G. Polymer, 1996, 37, 359.

68. Soares, D.A.W; de Souza, P. H. O; Rubinger, R. M; de Queiroz, A.A.A; Higa, O.Z and de Souza, L.R Brazilian Journal of Physics, 2004, vol. 34, no. 2B.

69. Yan,GL; Kuramoto, N and Takeishi, M Polym. Adv. Technol. 2003 14, 428.

70. Ita,M; Uchida,Y and Matsui,K. Journal of Sol-Gel Scienceand Technology, 2003,26, 479.

71. Ghosh,S. Macromolecules 1995,28, 4729.

72. Estrada,R.H.C; Folkes, M. J. Journal of Materials Science Letters, 2002,21, 1431

73. Ghosh, P;Sarkar, A; Ghosh, M; Meikap, A.K. Chattopadhyay, S.K;Chatterjee, S.K. Czech. J. Phys. 2003,53.

74. Cao, Y; Andreatta, A; Heeger, A. Jand Smith, P. Polymer, 1989, **30** () 2305.

75. Yasuda, A.and Shimidzu, T. Polymer J. 1993, **25** () 329.

76. Sun, Z; Geng, Y; Li, J; Wang, X; Jing, X and Wang, F . J. Appl. Polym. Sci. 1999, 72,1077.

77. Armes, S. P and Aldissi, M. Ibid. 1991, 32,2043.

78. Palaniappan,S; Saravanan,C; Amarnath,CA and Rao,VJ; Catalysis Letters 2004, Vol. 97, Nos. 1-2.

79. Ram,M.S; Palaniappan,S. Journal of Materials Science, 2004, 39 3069.

80. Pron, A.; Genoud, F ; Menardo, Cand Nechtschein, M. Ibid. 1988, 24 () 193.

81. Tsotcheva, D. ; Tsanov, T; Terlemezyan, L and Vassilev, S. Journal of Thermal Analysis and Calorimetry, 2001, Vol. 63, () 133.

82. Vecino, M. Gonzalez, I; Munoz, M. E; Santamarýa, A; Ochoteco, E and Pomposo, J. A. Polym.Adv.Technol. 2003, 14, 428.

83. Yawn,H; Sada,N and Toshima,N. Journal of Thermal Analysis and Calorimetry, 2002, Vol. 69 881.

84. de Farias, R. F and Nunes, L. M. Journal of Thermal Analysis and Calorimetry, 2002, Vol. 70, 559.

85. Xue, H; Shen, Z and Zheng, H. Journal of Applied Electrochemistry, 2002, 32: 1265.

86. Jun,J.B, Lee, C.H, Kim,J.W, Suh, K.D. Journal of Polymer Science: Part B: Polymer Physics, 2002, Vol. 40, 1163.

87. Lu,J and Zhao,X. J. Mater. Chem., 2002, 12, 2603.

88. Cho, M. S; Lee, J. H; Choi, H. J. Journal of Materials Science, 2004, 39,1377.

89. Jhon, M. S; Choi, H. J; Lee, Y. H; Kim, C. A. Journal of Materials Science Letters, 2000, 19, 533.

90. Levy,O and Stroud,D. J. Phys.: Condens. Matter, 1997, 9 L599.

91. Narula,A.K; Singh,S and Chandra,S. Bull. Mater. Sci., 2000, Vol. 23, No. 3,pp. 227.

92. Ito K, Tanabe Y, Akagi K and Lancaster M 1992 Phys. Rev.B45 1246

93. Anasuya Raghunathan, P. K. Kahol, and J. C. Ho Y. Y. Chen, Y. D. Yao, and Y. S. Lin B. Wessling Physical Review B 15 December 1998-Volume 58, Number 24

94. P. Dutta, S. Biswas, S.K. De, Mater. Res. Bull. 37 (2002) 193.

95. Y. Rao, S. Ogitani, P. Kohl, C.P. Wong, J. Appl. Polym. Sci. 83 (2002) 1084.

96. Y. Rao, C.P. Wong, Novel uitra-high dielectric constant polymer based composite for embedded capacitor application, in: Proceedings of the Polytronic 2002, the 2nd International Conference on Polymers and Adhesive in Microelectronics and Photonics, Zalaegerszeg, Hungary, 23-26 June 2002.

97. Ching-Piou Chwang , Cheng-Dar Liu , Sung-Wei Huang, Dean-Yang Chao, Sung-Nung Lee Synthetic Metals 142 (2004) 275-281

98. Thirumalizai Jambulingam Bhoopathy Annamalai Anandavadivel Mat Res Innovat (2002) 6:242.246

99. Rajendran S, Uma T (2000) Bull Mater Sci 23: 27

100. Kwarg S, Suh, Ho GyuYoon, Chang Ryong lee, Okamoto T,Takada T (1999) IEEE Trans on dielectric electrical Insulations 6: 284

101. Mirabel Cerqueira Rezende_, In´acio Malmonge Martin__, Roselena Faez Revista de F´ysica Aplicada e Instrumentac¸˜ao, vol. 15, no. 1, Dezembro, 2002.

102. RJ Sengwa. Polym Int 52:1462-1467 (2003)

103. RJ Sengwa, Rakhee Chaudhary and Kulvinder Kaur Polym Int 49:1308-1313 (2000)

104. Baur ME and Stockmayer WH, J Chem Phys 43:4319 (1965).

105. Yano S, Rahalkar RR, Hunter SP, Wang CH and Boyd RH, J Polym Sci Polym Phys Ed 14:1877 (1976).

106. Varadarajan K and Boyer RF, Polymer 23:314 (1982).

107. Johari GP and Monnerie L, J Polym Sci Polym Phys 1986 B 24:2049.

108. Johari GP, Polymer 1986, 27:866.

109. Beevers MS, Elliott DA and Willams G, Polymer 1980, 21:13.

110. Schonhal A and Stauga R, J Non-Cryst Solids 1998, 235±237:450.

111. Carini G, Crupi V, D'Angelo G, Majolino D, Migliardo P and Mel'nichenko YuB, J Chem Phys 1997, 107:2292.

112. Kimura H, Aikawa K, Masubuchi Y, Takimoto J, Koyama K and Uemura T, J Chem Phys 1997, 107:5945.

113. Mariz, J; Neto, G; Leal Ferreira, G. F; Santos,JR; Jr.,H. N. da Cunha, Dantas, I. F. and Bianchi,RF. Brazilian Journal of Physics, 2003, vol. 33, no. 2.

114. X. Duan, Y. Huang, Y. Cui, J. Wang and C. M. Lieber, Nature, 2001, 409, 66; D. Normile, Science, 1999, 286, 2056; J. Kong, N. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho and H. Dai, Science, 2000, 287, 622.

115. C. R. Martin, L. S. Van Dyke, Z. Cai and W. Liang, J. Am. Chem. Soc., 1990, 112, 8976; V. P. Menon, J. Lei and C. R. Martin, Chem. Mater., 1996, 8, 2382.

116. S. Demoustier-Champagne and P.-Y. Stavaux, Chem. Mater., 1999, 11, 829; M. Fu, Y. Zhu, R. Tan and G. Shi, Adv. Mater., 1996, 13, 1874; K. Kim and J. Jin, Nano. Lett., 2001, 1, 631.

117. K. Huang and M. Wan, Chem. Mater., 2002, 14, 3486; Z. Zhang, Z. Wei and M. Wan, Macromolecules, 2002, 35, 5937.

118. Y. Yang and M. Wan, J. Mater. Chem., 2001, 11, 2022; S. Youqing and M. Wan, J. Polym. Sci.: Part A: Polym. Chem., 1999, 37, 1443.

119. Jyongsik Jang And Hyeonseok Yoon Chem. Commun., 2003, 720–721

120. A.Mani, S. Tamil Selvan, K. L. N. Phani, S. Pitchumani Journal Of Materials Science Letters 17 (1998) 385-387

121. Wan,M and Li,J. Journal Of Polymer Science: Part A: Polymer Chemistry, 1999, Vol. 37, 4605.

122. Cai, Z.; Martin, C. R. J. Am Chem Soc 1989, 111,4138.

123. Cai, Z.; Lei, J.; Liang, W.; Menon, V.; Martin, C. R. Chem Mater 1990, 3, 960.

124. Liang, W.; Martin, C. R. J Am Chem Soc 1991, 112, 9666.

125. Parthsarathy, R. V.; Martin, C. R. Chem Mater1994, 6, 1627.

126. Mennen, V. Synth Met 1993, 55, 1165.

127. Martin, C. R.; Parthsarathy, R.; Menon, V. Synth Met 1993, 55, 1165.

128. Brumlik, C. J.; Martin, C. R. J Am Chem Soc 1991,113, 3174.

129. Huang, J.; Wan, M. J Polym Sci 1999, 37, 151.

130. Wang,Q; Wan,W. Journal of Materials Science Letters 2000, 19, 1645.

131. Xia,H and Wang,Q. Journal of Nanoparticle Research 2001, 3: 401.

132. Boutonnet M., J. Kizling, P. Stenins & G. Marie Colloids and Surfaces 1982. 5, 209.

133. Kortan A.R., Hull, R. Opila, R.L ; Bawendi, M.G ; Steigerwald, M.L ; Carroll, P.J and Brus, L.E J. Am. Chem.Soc. 1990,112, 1327.

134. Pileni M.P., Motte, L and Petit, C. Chem. Mater. 1992, 4, 338.

135. Candau F., Long, Y.S;Pouyet, Gand Candau, S.J. Colloid Interface Sci. 1984, 101, 167.

136. Gan L.M., Chew, C.H; Chen, H.S.Oand Ma, L. Polymer Bull. 1993, 31, 347.

137. Markham G., Obey T.M. and Vincent, B.Colloids and Surfaces 1990, 51, 239.

138. Gan L.M., S.C. Ng, S.P. Ong, C.H. Chew & L.L. Koh, 1989.

139. Selvan S.T., A. Mani, K. Athinarayanasamy, K.L.N. Phani & S. Pitchumani, 1995. Mater. Res. Bull. 30, 699.

140. Wang Q., H.S. Xia & C.H. Zhang, 2001. J Appl. Polym. Sci. 80,1478.

141. Xia H.S., Wang, Q. and Zhang, C.H. J Appl. Polym. Sci. 2001, 80, 1130.

142. Malecki, J. and Hilczer, B. Key Engineering Materials, 1994, **92-93**, p. 181

143. Joo, J ; Oblakowski, Z ; Du, G ; Pouget, J. P ; Oh, E.J ; Wiesinger, J. M ; Min, Y ; MacDiarmid, A.G and Epstein, A. J. Phys. Rev. B, Rapid Comm., 1994, **49** p. 2977.

144. Youngs, J; Lawrence, C. R; Treen, A. S; Stickland, T; Miah, M. IEEE Proc-Sci. Meas. Technol., 1998, **145** p. 166.

145. Naishadham, K. Chandrasekhar, P and Meixner, R. Microwave Symposium Digest, IEEE MTT-S International **3**, 1998, p. 1353.

146. Obrzut, J.and Chiang, C. K. Mat. Res. Soc. Symp. Proc. Vol. 576

147. Walpita, L. M.; Pleban, W. M.; Eckhardt, H. U.S. Patent5,962,122, Oct 5, 1999.

148. Jones, F. G.; Shrout, T. R.; Jang, S. J.; Lanagan, M. T.Applications of Ferroelectrics, 1990, 7th International Symposium on Applications of Ferroelectrics, p 455.

149. Walpita, L. M.; Ahern, M. R.; Chen, P.; Goldberg, H.; Hanley,S.; Pleban, W. M.; Weinberg, S.; Zipp, C.; Adams, G.; Wong,Y. H. IEEE Trans. Microwave Theory Tech. 1999, 47, 1577.

150. Truong, V. T.; Codd, A. R.; Forsyth, M. J. Mater. Sci. 1994,29, 4331.

151. Obrzut, J.; Nozaki, R. Proceedings of the IPC EXPO Technical Conference, April 2-8, 2000, San Diego, CA.

152. Popielarz, R; Chiang, C. K; Nozaki, R and Obrzut, J. Macromolecules 2001, 34, 5910.

Chapter 2

Experimental Techniques

The materials used and the experimental procedures adopted in the present investigations are detailed in this chapter.

2.1. MATERIALS USED

2.1.1 Materials used for the preparation of conducting polymers

1. **Aniline**

Aniline used for the synthesis is AR grade, supplied by E.Merck (P) Ltd., Mumbai, having the following specifications:

Boiling point - 182-185 ^{0}C

Assay(GC) - 99%

Density(g/cc) - 1.02-1.022

2. ***o*-Anisidine**

o-Anisidine used for the synthesis is AR grade, supplied by Merck laboratories (P) Ltd., Mumbai.

3. ***o*-Toluidine**

o-Toluidine used for the synthesis is AR grade, supplied by SISCO research laboratories (P) Ltd., Mumbai, having an assay of 98%.

4. **Ammonium Per sulphate**

Ammonium persulphate [Extra pure][M=228.20g/mol] used for the synthesis is AR grade, supplied by SISCO Research Laboratories (P) Ltd., Mumbai, having an assay of 98%.

5. **Acetone**

Acetone used in the present study is AR grade, and was supplied by S.D.Fine-CHEM Ltd., Mumbai having boiling point of 65 ^{0}C and density of 0.7866 g/cm^3

6. **Methanol**

Methanol used in the present study is AR grade, and was supplied by S.D.fine-CHEM Ltd., Mumbai having boiling point of 65^{0}C and density of 0.7866 g/cm^3.

2.1.2 Dopants Used

1. **Hydrochloric acid**

Hydrochloric acid used is LR grade, having an assay (acidimetric) of 35-38 %, supplied by E. Merck (India) Ltd., Mumbai.

2. **Perchloric acid**

Perchloric acid used is 60 %, LR grade, supplied by Citra Diagnostics, Kochi.

3. **Nitric acid**

Nitric acid used is LR grade, having an assay (acidimetric) of 69-72 %, supplied by S.D.fine-CHEM Ltd., Mumbai.

4. **Sulphuric acid**

Sulphuric acid used is LR grade, supplied by S.D.fine -CHEM Ltd., Mumbai.

5. **Camphor sulphonic acid**

Camphor sulfonic acid (98%) used is supplied by S.D.fine -CHEM Ltd., Mumbai.

6. **Toluene sulphonic acid**

Toluene sulfonic acid (98.5 %) is obtained from S.D.fine -CHEM Ltd., Mumbai.

7. **β- naphthalene sulphonic acid/Naphthalene- 2- sulphonic acid**

β- naphthalene sulphonic acid/ Naphthalene- 2-sulphonic acid[98%] used is supplied by SISCO Research Laboratories Pvt.Ltd.

8. **D-Glucose**

D-Glucose [anhydrous] Specific rotation $[\alpha]_D^{20^\circ}$ = +52° to +53° used is supplied by Qualigens Fine Chemicals, Mumbai.

9. Sucrose

Sucrose pure [M=342.30g/mol] used is supplied by Merck limited, Mumbai

10. D(+)Mannose

D(+)Mannose used is supplied by LOBA CHEMIE Pvt.Ltd, Mumbai

11. Oleic acid

12. Ammonia Solution

2.1.3 Polymers

1. Poly(vinyl chloride) (PVC)

Poly(vinyl chloride) used is Emulsion grade having the K value 70.5, supplied by Chemplast, Madras.

2. Rubber Chemicals

Naphthenic oil used was commercial grade

3. Fillers :

i. Ultrafine silica[U-sil] :commercial grade

ii. VN3

VN3 grade of silica has the following specifications:

Surface area (m^2 g^{-1}) - 175

Bulk Density [g/l] - 252

Moisture - 5.7

iii. Precipitated silica supplied by Degussa, Germany, has the following specifications:

Surface area (m^2 g^{-1})	-	234
Oil absorption (g per 100 g)	-	240
Mean particle diameter (nm)	-	20

2.2 EXPERIMENTAL METHODS

2.2.1 Preparation of different forms of conducting polymers

Conducting polymers were prepared by chemical methods and the semi interpenetrating polymer networks were prepared by the in-situ polymerization technique. Polymers were prepared as pellets for dielectric property measurements.

1. Pellet form

The conducting polymers prepared by the chemical method was filtered, washed and oven dried (at 50 - 60 °C, 6h). The polymer in the powder form was taken in a die of diameter 5mm and pressed under a hydraulic press at a constant pressure of 2.5 tons into a pellet. The pellet was carefully removed from the die and the dielectric properties were measured.

2.3 PHYSICAL TEST METHODS

2.3.1 Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectra are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm^{-1} by organic molecules. Different functional groups and structural features in the molecule absorb at characteristic frequencies. The frequency and intensity of absorption are the indication of the bond strengths and structural geometry in the molecule. FTIR spectra of the samples were recorded on a Nicolet Avtar 360 ESP FTIR spectrometer.

2.3.2 *Thermogravimetric analysis (TGA)*

Thermogravimetric analysis is carried out in a TGA Q50 (TA) at a heating rate of 5 °C/minute. Thermograms are recorded from room temperature to 800 °C. The onset of degradation temperature, the temperature at which the rate of weight loss is maximum (T_{max}), and the residual weight in percentage are evaluated. Sample size was between 5 and 10 mg.

2.3.3 *Differential Scanning Calorimetry (DSC)*

DSC is used to investigate thermal transitions including phase changes, crystallization, melting or glass-rubber transitions of a material as a function of temperature. Heat flow corresponding to either heat absorption (endothermic) or heat emission (exothermic) of the sample per unit time is measured with respect to a reference. TA Instrument (DSC Q 100) equipped with a RCS cooling system is used to study thermal transitions in the samples at a heating rate of 5°C/min. The sample size was between 7 and 10mg.

2.3.4 *Scanning Electron Microscopy*

Scanning electron microscope (SEM) is a very useful tool in polymer research for studying the morphology of powder form of conducting polymers. In this technique, an electron beam is applied across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X-rays. These signals are monitored by detectors (photomultiplier tube) and magnified. An image of the investigated microscopic region of the specimen is thus observed in cathode ray tube (CRT) and photographed using photographic film. In the present investigation, a JEOL JSM-840 model-6211 (Oxford, England) was used to study the morphology of various conducting polymers.

2.3.5 *Measurement of microwave properties - Cavity perturbation technique*[1]

In the cavity perturbation technique generally rectangular or cylindrical waveguide resonators are employed. When a dielectric material is introduced into a cavity resonator at the position of maximum electric field, the resonant frequencies of the cavity are perturbed. The contribution of magnetic field towards the perturbation is minimum at this position. So from the measurement of the perturbation due to the sample, the dielectric parameters can be determined. The availability of sweep oscillators and network analyzer makes it possible to measure the dielectric parameters at a number of frequencies in single band.

2.3.5.1 Design of rectangular waveguide cavities

The cavity resonators are constructed from brass or copper wave-guides. The S-band rectangular waveguide cavity resonator is constructed from a section of standard WR-284 wave-guide. The inner walls of each cavity are silvered to reduce the wall losses. All the three resonators are of transmission type, since power is coupled into/out through separate irises. The amplitude response of a typical cavity at S-band is shown in figure 2.1.

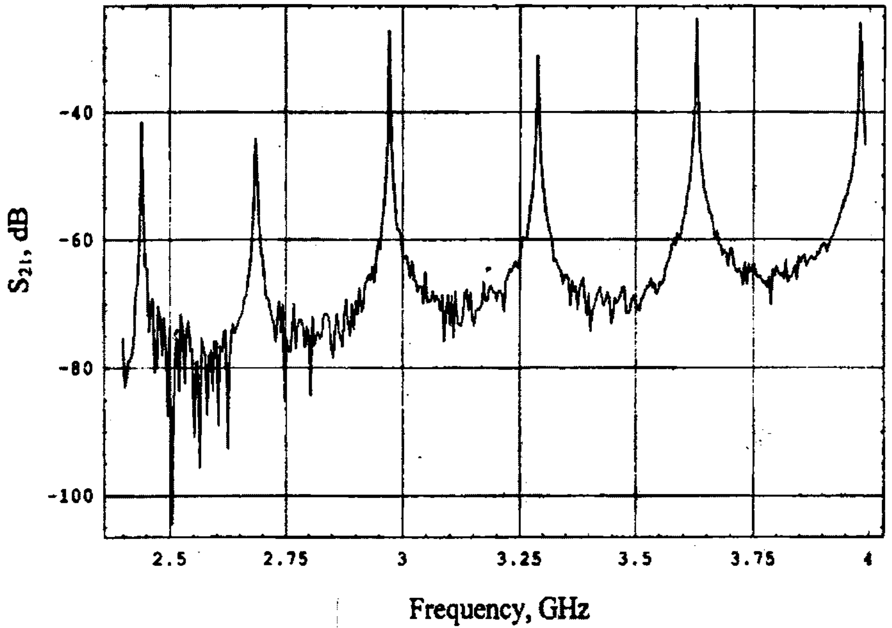


Fig.2.1: Resonance frequency spectrum.

Table 2.1 shows the design details of S band rectangular waveguide cavity[2] and table 2.2 shows the resonant frequencies and the Q factors of the cavities used.

Dimensions of the cavity(mm)	S band
Length, d	353
Breadth, a	72
Height, b	33.5
Diameter of the coupling hole	12.8
Length of the slot on the broad wall	225
Width of the slot	4

Table 2.1:Design parameters of S band rectangular waveguide cavity.

Type of cavity	Resonant frequencies (GHz)	Q-factor
S-band cavity	2.4397	4879
	2.6833	5366
	2.9692	3711
	3.2853	2986
	3.6237	2001

Table 2.2 Resonant frequencies and Q factor values of S band cavity.

The schematic diagram of a typical transmission type cavity is shown in the figure 2.2.

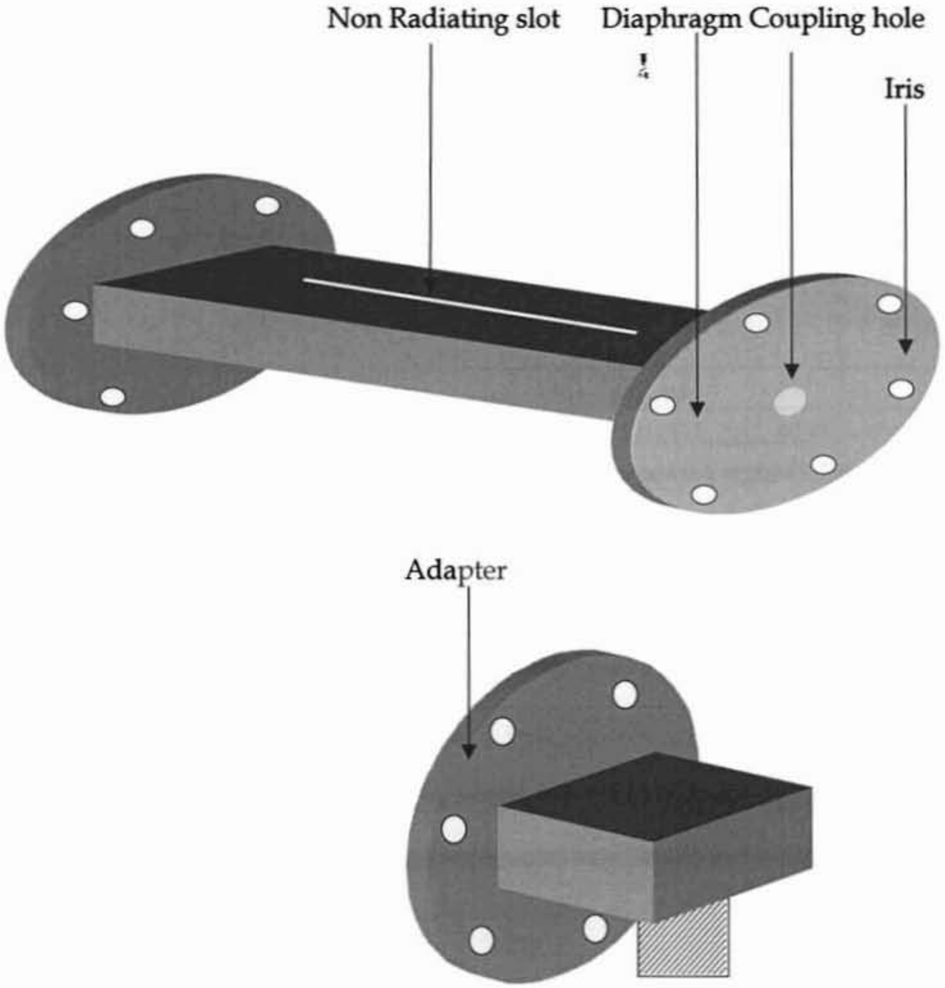


Fig.2.2: Schematic diagram of a typical cavity resonator

2.3.5.2 Setup and theory

The experimental setup[3] consists of an HP8510 vector network analyser; sweep oscillator, S - parameter test set and the rectangular cavity resonator.

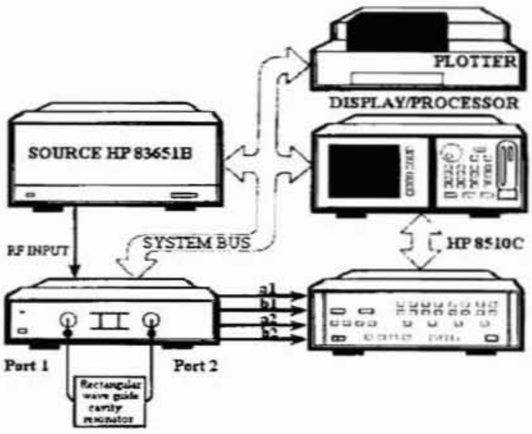


Figure.2.3 : Experimental setup

The measurements were done at 25 C in S band (2 GHz - 4 GHz). The field perturbation inside the cavity is given by Kupfer et al[4].

$$-\frac{d\Omega}{\Omega} \approx \frac{(\bar{\varepsilon}_r - 1)\int_{V_s} E \, . \, E_0^* \, dV}{2\int_{V_c} \left| E_0 \right|^2 dV} \qquad (1)$$

where $d\Omega$ is the complex frequency shift. V_c and V_s are the volumes of the cavity and sample respectively. E and E_0 are the perturbed and unperturbed fields in the cavity. ε_r^* is the relative complex permittivity of the sample material. Complex frequency shift is related to the quality factor, Q as

$$\frac{d\Omega}{\Omega} \approx \frac{d\omega}{\omega}+\frac{j}{2}\left[\frac{1}{Q_s}-\frac{1}{Q_0}\right] \qquad (2)$$

Q_s and Q_o are the quality factors of cavity with and without sample. Quality factor Q is given by Q = f / Δf where f is the resonant frequency and Δf is the corresponding 3dB bandwidth. For small samples we assume that $E = E_0$ and for dominant TE_{10p} mode in a rectangular wave guide,

$E_0 = E_{0max}\sin(\pi x/a)\,\sin(\pi pz/d)$, p=1,2,3...... (3)

From equations (1) to (3) the real and imaginary parts of the relative complex permittivity are given by

$$\varepsilon_r^{\prime} = 1+\frac{f_o-f_s}{2f_s}\left(\frac{V_c}{V_s}\right) \qquad (4)$$

$$\varepsilon_r^{\prime\prime} = \frac{V_c}{4V_s}\left(\frac{Q_o-Q_s}{Q_oQ_s}\right) \qquad (5)$$

The real part of the complex permittivity, ε'r is generally known as dielectric constant and the imaginary part ε''r of the complex permittivity is related to the dielectric loss of the material.

The loss tangent is given by,

tan δ = loss current/charging current = ε''r / ε'r (6)

where ε' is the measured dielectric constant of the dielectric material and ε'' is the loss factor or loss index.

Here $\sigma + \omega\varepsilon''_r$ is the effective conductivity of the medium. When the conductivity σ due to free charge is negligibly small (good dielectric) the effective conductivity is due to electric polarization and is reduced to

$$\sigma_e = \omega\varepsilon''_r = 2\,\pi\,f\,\varepsilon_0\,\varepsilon''_r \qquad (7)$$

The efficiency of heating is usually compared[5] by means of a comparison coefficient J, which is defined as

$$J = 1/\varepsilon_r \tan\delta. \qquad (8)$$

The absorption of electromagnetic waves when it passes through the medium is given by the absorption coefficient[6] (α_f), which is defined as,

Absorption coefficient (α_f) = $\varepsilon''_r\, f / n\ c$ (9)

Where n= ε^* and 'c' is the velocity of light.

Penetration depth (also called as skin depth) is basically the effective distance of penetration of an electromagnetic wave into the material[7],

Skin depth (δ_f)= $1 / \alpha_f$ (10)

2.3.6. Measurement of dielectric parameters in the High Frequency Field [.05-13 MHz]

The conductivity at low frequencies is measured using HP 4192 Impedance analyzer.

Specifications of the analyser is shown below:

Frequency - 5 Hz to 13 MHz

Measuring range - .001 M to 1.2999 M with a resolution of 100 μ

Phase range - -180.00^0 to +180.00^0 with a resolution of .01^0

The resistance of the material at different frequencies (from .05MHz to 13 MHz) in pellet form is determined from impedance analyzer and then the conductivity is calculated using the equation;

Loss Tangent and Capacitance is directly obtained from the measurements.

The dielectric constant can be calculated using the formula

$$\text{Dielectric constant } K = \frac{\text{capacitance. } T \,.\, 10{,}000}{.0885 \,.\text{Area}}$$

Area in mm2

T - Thickness of the sample in mm

Capacitance in nF

Conductivity $[\sigma] = 2\,\pi\, f\, \varepsilon'\, \varepsilon^{o} \tan\delta$

2.4 REFERENCES

1. K. T. Mathew, U. Raveendranath, *Sensors Update*,**(1998)** Baltes, H.; Gopel, W.; Hesse, J. Eds. WILEY-VCH (UK)
2. U.Raveendranath, *Ph.D. thesis:* chapter 3. ,**(1996),** Department of electronics, Cochin University of Science and Technology, Kerala
3. K.T.Mathew and U.Raveendranath, *Waveguide cavity Perturbation method for measuring complex permittivity of water, Microwave and Optical Technology Letters* USA ,**(1993)** Vol.6, No.2, pp. 104
4. K .Kupfer, A. Kraszewski, and R.Knochel, *Sensors update* ***Vol.7*** *& Microwave sensing of Moist materials, Food and other Dielectrics*. **(2000)**.Wiley-VCH, Germany,186
5. Chen. C. Ku; Raimond Liepins, *Electrical Properties of Polymers: Chemical Principles*, **(1987),** Hanser Publishers: Munich.
6. L. S.Bradford, M.H. Carpentier,*The Microwave Engineering hand book*, Chapman and Hall, **(1993)**, London
7. C. W. Stephen, H. L.Frederic, Microwaves *made simple: principles and applications*, , **(1985),** United States Bookcrafters, Chelsea.

Chapter 3

Optimization of preparation conditions on the dielectric properties of polyanilines

3.1 INTRODUCTION

Since the first report of metallic conductivities in "doped" polyacetylene in 1977[1] the science of electrically conducting polymers has advanced very rapidly. More recently, as high-purity polymers have become available, application of conducting polymers as integral components in a range of semiconductor devices has been investigated. These include transistors[2-5], photodiodes[6-7], and light-emitting diodes (LEDs)[8-10]. The potential for commercialization is perceived to be high for these polymer-based semiconductor devices because they compete in application areas where the market can bear the costs of development. In particular, polymer LED's shows attractive device characteristics, including efficient light generation. Consequently, several development programs are now being set up to establish procedures for their large-scale manufacture. The principal interest in the use of polymers lies in the scope for low-cost manufacturing, using solution processing of film-forming polymers. In parallel with these development activities, much progress has been made in the understanding of the underlying science that controls the properties of these devices. In comparison with inorganic semiconductors, relatively little is known about the electronic properties of these materials; even the nature of the semiconductor excitations remains controversial. Considerable progress made in resolving some of the issues that determine the limits to device performance, and there have been several recent reviews[11-13]. Friend et al[14] have published a comprehensive review on the progress made in the use of conjugated polymers in LEDs and in photovoltaic diodes.

In this chapter we report the preparation, structural analysis, dielectric characterization [2-4 GHz] and thermal behavior of polyaniline and it analogues like poly (*o*-toluidine) and poly (*o*-anisidine). The behaviour of these conducting systems has been evaluated in the High Frequency field of .05MHz-13MHz. The effects of reaction temperature and dopants on the microwave properties of these polymers are elaborated. The effect of both organic and inorganic dopants has also been studied. Cavities operating at S band are used for the characterization of the samples pelletised under 2.5 tonnage pressure. To adhere to accuracy limits, the volume of the sample has been maintained at 1/1000th of the volume of the cavity used. An optimization has been carried out based on this preliminary line of study.

PART I

3.2 STUDIES ON POLYANILINE

3.2.1 INTRODUCTION

Polyaniline (PAni) is one among the most intensively investigated conducting polymers. The establishment of the scientific principles allowing regulation of its properties, determining the potential application areas (alternative energy sources and transformers, media for erasable optical information storage, non-linear optics, membranes, etc.) is an important scientific problem. Both the polymerization of aniline and the subsequent transformations of polyaniline have to be regarded as typical redox processes, where the direction and establishment of equilibrium are dependent on the oxidation potentials and concentrations of the reactants (and also on pH of the medium). On the other hand, although some manufacturers have put a lot of effort into the development of some applications of this material, there exist too many ambiguities about PAni. They are related to both the mechanism of polymerization and the polymer structure (including its transformations), in determining the material properties.

PAni has been investigated extensively and attracted interest as a conducting material for several important reasons; the monomer is inexpensive, the polymerization reaction is straightforward and proceeds with high yield, and PAni has excellent stability. The most significant findings of the investigations on PAni, presented most comprehensively in the review articles [15-23], are summarized in the following picture. PAni exists in three well-defined oxidation states: leucoemeraldine, emeraldine and pernigraniline (Figure 3.1). Leucoemeraldine and pernigraniline are the fully reduced (all the nitrogen atoms are amine) and the fully oxidized (all the nitrogen atoms are imine) forms, respectively, and in emeraldine the ratio is ~0.5. As shown by Alan MacDiarmid and his collaborators in the mid-80s, polyaniline can be rendered conducting through two independent routes: oxidation (either chemically or electrochemically) of the leucoemeraldine base or protonation of the emeraldine base through acid-base chemistry. Because the insertion of counterions is involved in both routes, conducting polyaniline may be regarded as a polycation with one anion per repeat unit. Thus it is clear that starting from the electrically insulating leucoemeraldine, electrically conducting emeraldine can be obtained by standard chemical or electrochemical oxidation, as with other conducting polymers. But, upon further oxidation of emeraldine, a second redox process occurs, which yields a new insulating material, pernigraniline.

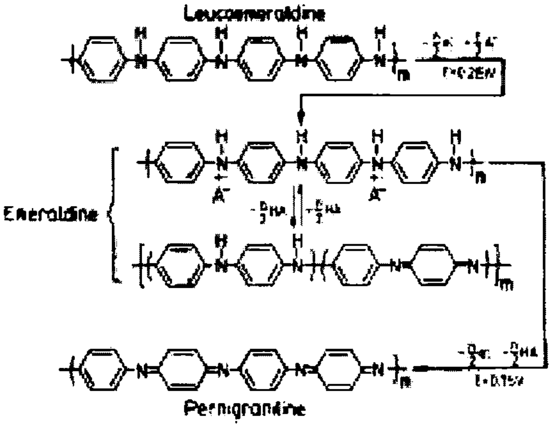


Figure 3.1: The different oxidation states of Polyaniline

PAni and its analogues have generated tremendous interest among scientists and technologists due to their wide variety of desirable properties and potential technological applications. Of particular interest is the very large capacity of PAni to absorb and reflect electromagnetic radiation by changing its dielectric constant on interaction with energy of radiowave-microwave millimeter wave range[24-26]. This makes PAni an appropriate candidate to shield electromagnetic interference where PAni approaches the shielding efficiency of copper[24,27-30], in the design of microwave absorbers for stealth purposes and in areas involving remote heating of materials and surfaces e.g. joining of plastics[24,31,32]. Dependence of the electric behavior of PAni on the frequency of the electric field and temperature[33-35] allows designing PAni-based materials, which are effective in a defined temperature-frequency range both possible and attractive. In addition to this unusual behavior, a decrease of conductivity by ten orders of magnitude is obtained just by treatment of the conducting emeraldine in neutral or alkaline media. Protonation induces an insulator-to-conductor transition, while the number of π-electrons in the chain remains constant. A lot of work has been devoted to unravel the mystery of this unusual transition. The mechanism of oxidative polymerization of aniline, which always results in a conducting emeraldine PAni, appears also to be ambiguous.

In this section the dielectric response of PAni prepared at different temperatures with both organic and inorganic dopants is described.

3.2.2 EXPERIMENTAL

- *Preparation of Polyaniline [Doped form -in situ polymerization]*

- **With inorganic dopants:** Chemical oxidative polymerisation of aniline to give the conducting emeraldine salt was carried out using ammonium persulphate as initiator in the presence of 1M HCl at 0-5 ° C [LT], room temperature [RT] and at 60°C [HT]. The reaction was carried out for 4h. The green precipitate formed was filtered washed with water, acetone and methanol. The samples were then oven dried at 50- 60 °C for 6h. The reaction was repeated with 1M solutions of different dopants like sulphuric acid, nitric acid and perchloric acid, with a view to determine the best dopant. The consequence of variation in molar concentration of the best dopant was then evaluated. The dielectric parameters were measured for the pelletised samples [2.5 tonnage pressure] using the cavity perturbation technique described in Chapter 2. The polymer formed was characterized using InfraRed [IR] spectroscopy, Thermogravimetric Analysis [TGA], Differential Scanning Calorimetry [DSC] and Scanning Electron Microscopy [SEM].

- **With organic dopants:** The polymerisation reaction was repeated with 1M solutions of organic dopants like toluene sulphonic acid, naphthalene sulphonic acid and camphor sulphonic acid.

- *Preparation of undoped polyaniline [PAni undoped]:* Chemical oxidative polymerisation of aniline was carried out using ammonium persulphate as initiator in the absence of any doping agents at room temperature. The reaction product formed was filtered out, washed with acetone and methanol. The polymer formed was oven dried (at 50- 60 °C) for 6h.

3.2.3 RESULTS AND DISCUSSIONS

3.2.3.1 Effect of polymerization condition and inorganic dopants on the dielectric properties

1. **Dielectric loss (ε″) and Conductivity (σ)**

Figures 3.2 and 3.3 show the effect of different dopants and the temperature of preparation at 0-5°C [LT], room temperature 28°C [RT] and at high temperature 60°C [HT] on the dielectric loss and conductivity of polyaniline at 2.97 GHz. It is clear from the figurs that Polyaniline prepared at room temperature shows higher dielectric loss and conductivity in all cases. In the microwave field the dielectric loss occurs due to the dipolar polarization. The dipolar polarization in an a.c. field leads to dielectric relaxation due to orientation polarization. Dielectric relaxation[36] is the lag in dipole orientation behind an alternating electric field and under the influence of which the polar molecules of a system rotate toward an equilibrium distribution in molecular orientation with a corresponding dielectric polarization and thus results in the generation of dielectric loss. When the polymerization temperature of aniline is increased, head to head [benzene to benzene] sequence of Polyaniline is greater compared to head to tail sequence [NH to benzene], which reduces the conjugation length of Polyaniline, and in turn reduces the intrachain conduction. Since the intrachain conduction is more compared to the interchain conduction, samples prepared at high temperature shows less dielectric loss[37]. Since the conductivity in the microwave field is directly related to the dielectric loss factor, the conductivity is proportionately higher for Polyaniline prepared at room temperature.

It is also clear from the figures that the dielectric loss and conductivity is highest for $HClO_4$ doped polyaniline followed by HCl-doped sample. When the polar group is large, or the viscosity of the medium is very high, the rotatory motion of the molecule is not sufficiently rapid for the attainment of equilibrium with the field. In the case of HCl dopant, the size is less when compared to all other dopants and hence it shows better relaxation phenomenon, which increases dielectric loss.

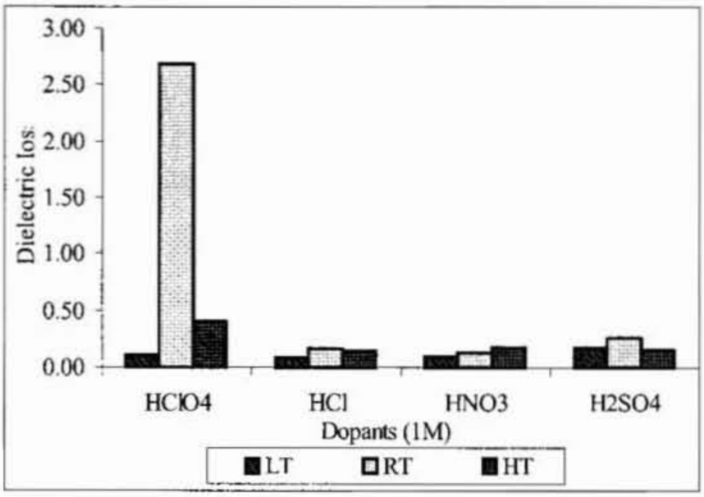


Figure 3.2: Effect of dopants and temperature on the dielectric loss at 2.97GHz

At the same time increasing the size of the counter ion leads to a material with conductive path having a higher doping level than small counter ions. This will increase the intrachain conductivity and since the intrachain conductivity contributes to an increase in dielectric loss than the interchain conductivity, the dielectric loss and conductivity of $HClO_4$ doped samples are higher than those of HCl and other inorganic acid doped samples.

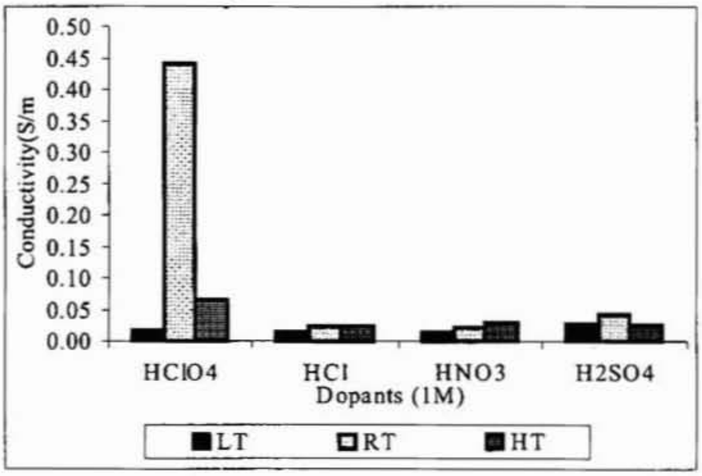


Figure 3.3: Effect of dopants and temperature on the conductivity at 2.97GHz

2. Dielectric constant (ε′)

Figure 3.4 shows the variation of dielectric constant of different doped samples at 2.97 GHz. It is clear from the figure that the dielectric constant of $HClO_4$ doped sample is low compared to samples with other dopants. When a field is applied, the positive charges move with the electric field and an equal number of negative charge moves against it, resulting in no net charge within the polymer. However, there is a net positive charge at the surface where the positive direction of the field emerges and a negative charge at the surface where the field enters. Thus, a large field outside it produces the field within the polymer, and the normal components have the ratio given by the dielectric constant.

When the size of the dopants are high, the inter chain distance between the polymer chains increase, which result in a decreased capacitive couplings and hence the dielectric constant is low.

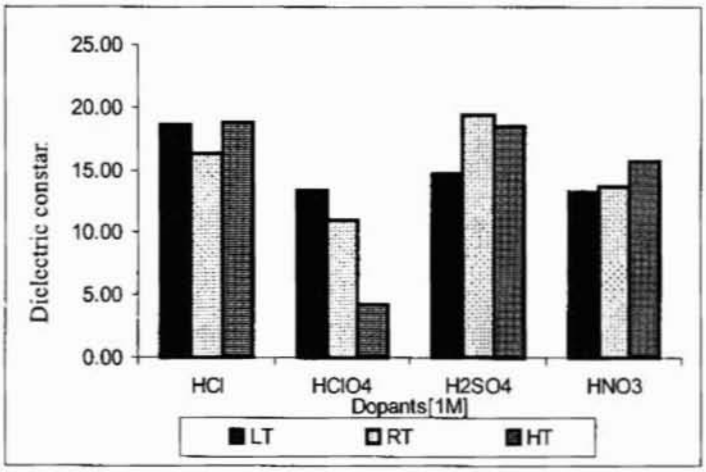


Figure 3.4: Effect of dopants and temperature on the dielectric constant at 2.97GHz

3. Dielectric heating coefficient (J)

Figure 3.5 shows the effect of different dopants on the dielectric heating coefficient of Polyaniline. It is clear from the figure that the dielectric heating coefficient is a minimum for $HClO_4$ doped sample prepared at room temperature. As the heat generation in polymers is due to relaxation loss, the efficiency of heating of a polymer is compared by means of a heating coefficient[38].

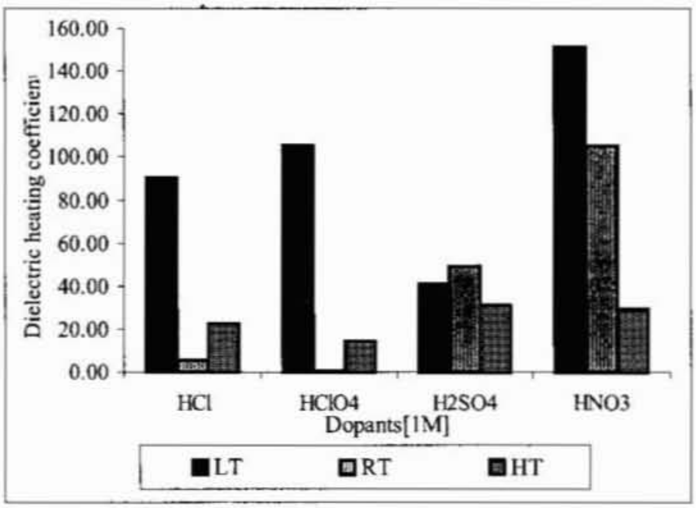


Figure 3.5: Effect of dopants and temperature on the dielectric heating coefficient at 2.97GHz

The dielectric heating coefficient is inversely related to the dielectric loss factor and hence the $HClO_4$ doped samples shows the minimum value. The higher the heating coefficient the poorer is the heating property.

4. Loss Tangent (tan δ)

Loss tangent of Polyaniline doped with different dopants is plotted in Figure 3.6. Loss tangent is the tangent of the angle δ between the vector for the amplitude of the total current and that for the amplitude of charging current[39]. As it is directly related to the dielectric loss, the loss tangent also shows the same behavior as that of dielectric loss.

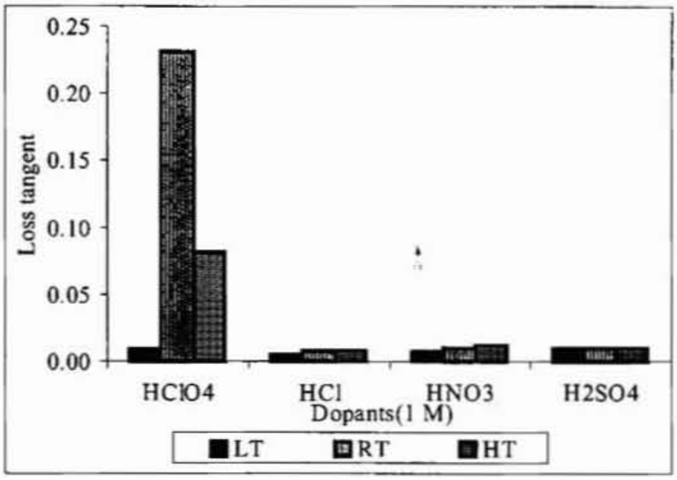


Figure 3.6: Effect of dopants and temperature on the Loss tangent at 2.97GHz

5. Absorption coefficient and Skin Depth

Figures 3.7 and 3.8 show the absorption coefficient and penetration depth of Polyaniline samples respectively. Absorption coefficient is derived from the complex permittivity and is a measure of the propagation and absorption of electromagnetic waves when it passes through a medium. The dielectric materials can be classified in terms of this parameter indicating the transparency of waves passing through it. The absorption coefficient is directly related to the dielectric loss factor and therefore it shows the same behavior as dielectric loss. It is clear from Figure 3.8 that the skin depth is low for $HClO_4$ doped Polyaniline prepared at room temperature. As the skin depth, also called penetration depth, is basically the effective distance of penetration of an electromagnetic wave into the material[40], it is inversely related to the absorption coefficient.

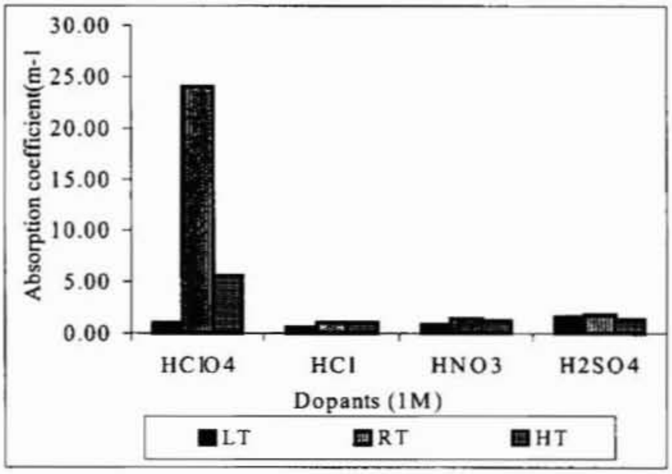


Figure 3.7: Effect of dopants and temperature on the Absorption coefficient at 2.97GHz

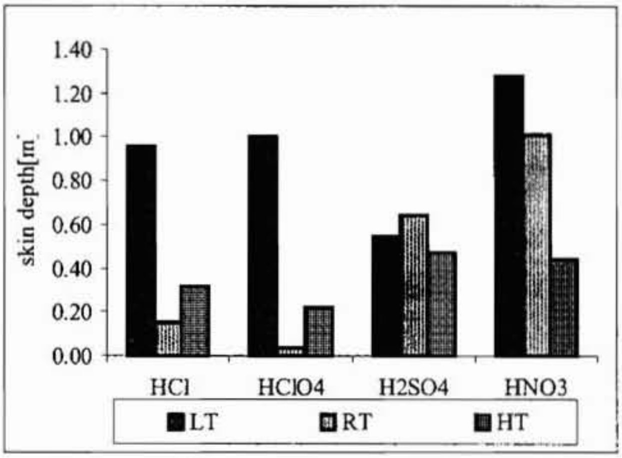


Figure 3.8: Effect of dopants and temperature on the skin depth at 2.97GHz

3.2.3.2 Effect of variation in molar concentrations of dopants on the dielectric properties

Since $HClO_4$ doped polyaniline was found to be the most promising one in the microwave field, variation of other parameters is carried with it. Figure 3.9 shows that conductivity and dielectric loss decrease with increase in the molarity of the acid. This can be attributed to the accumulation of charges thereby preventing an effective polarization of the doped polymer segments. The same trend is observed in the case of loss tangent and absorption coefficient of the $HClO_4$ doped Polyaniline samples, as shown in figure 3.10. The best property is observed for the 1M $HClO_4$ doped Polyaniline.

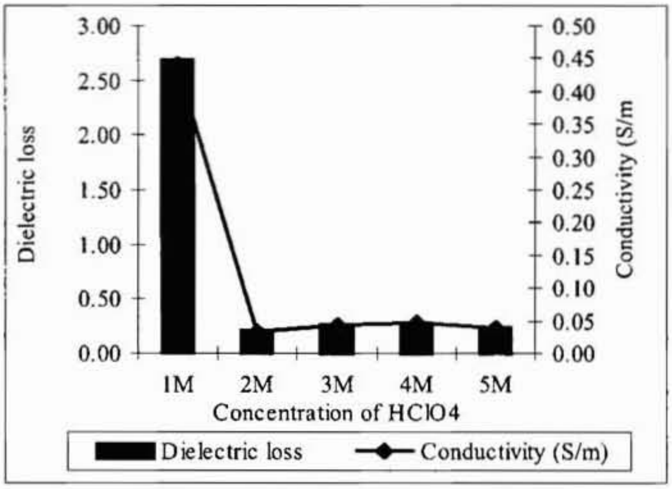


Figure 3.9: Variation of Dielectric loss and conductivity for $HClO_4$ doped PAni

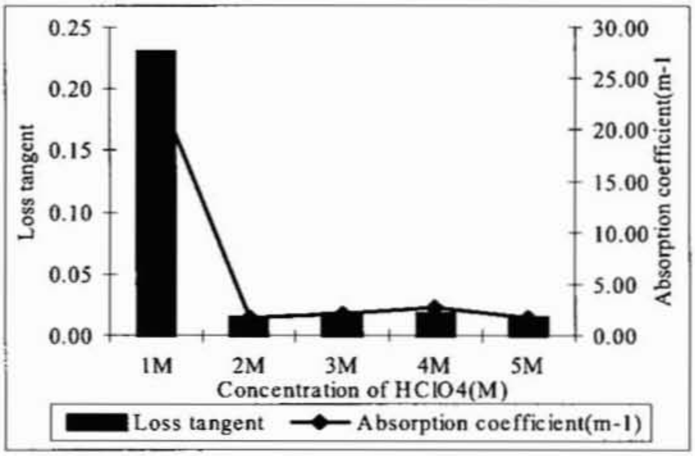


Figure 3.10: Variation of Loss Tangent and Absorption coefficient for $HClO_4$ doped samples

3.2.3.3 Characterization and dielectric properties of $HClO_4$ doped samples

I. Characterization

[i] IR spectroscopy

The IR spectrum of $HClO_4$ doped Polyaniline is presented in Figure 3.11 The peak at 3449 cm^{-1} indicates the presence of -NH stretching vibration and the peaks at 1238 cm^{-1}, 1117 cm^{-1}, 1108 cm^{-1}, 882 cm^{-1} are the characteristic frequencies of Polyaniline samples[41]. The peak at 1556 cm^{-1} indicates the presence of quinoid ring stretching vibration and the band at 1298 cm^{-1} indicates the presence of CN stretching vibration in polyaniline. All these findings confirm the formation of doped polyaniline samples in the presence of $HClO_4$.

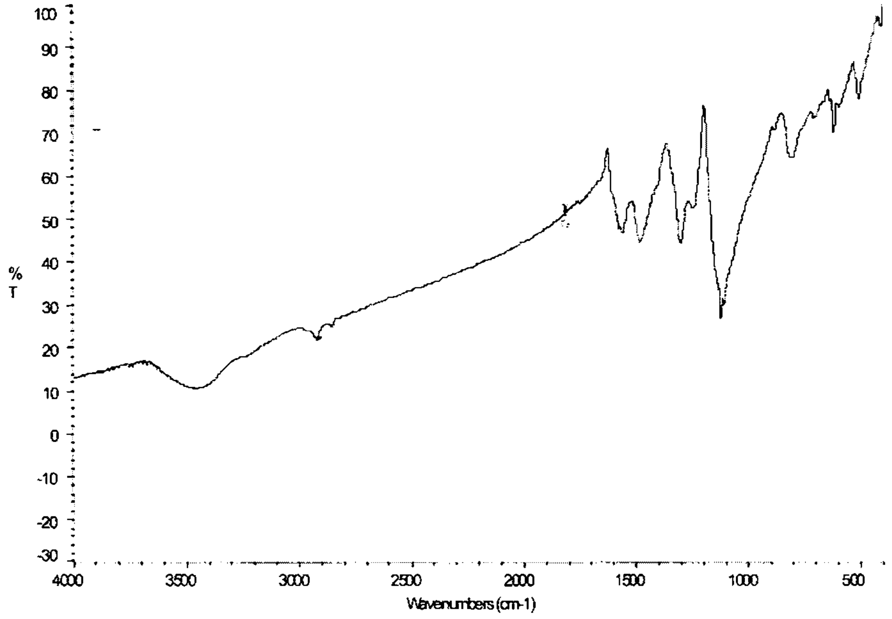


Figure 3.11: IR spectrum of $HClO_4$ doped Polyaniline

[ii] Thermal studies

Figures 3.12 and 3.13 show the TGA and DSC thermogram of $HClO_4$ doped Polyaniline samples. The TG curve indicates that there is a weight loss of 20% for polyaniline due to the evolution of $HClO_4$ dopant at 240°C. About 41% of weight loss at 550°C indicate the degradation of polyaniline chain. The DSC curve shows that the glass transition temperature (Tg) of polyaniline is 110 °C.

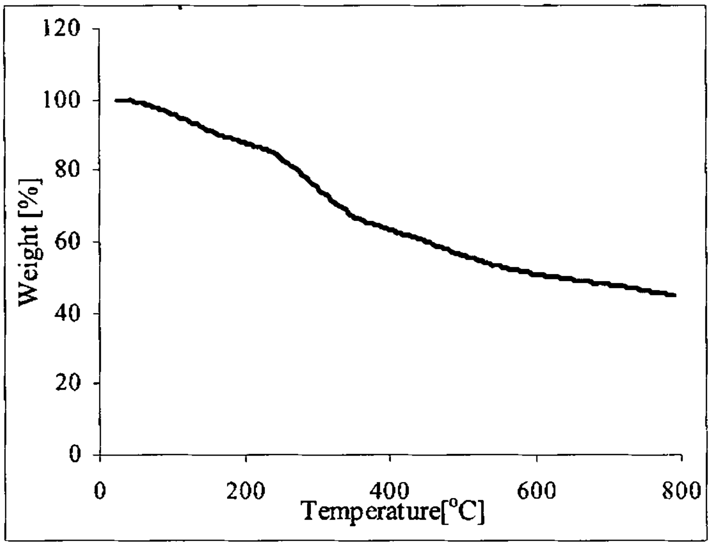


Figure 3.12: TGA thermogram of PAni [HClO$_4$]

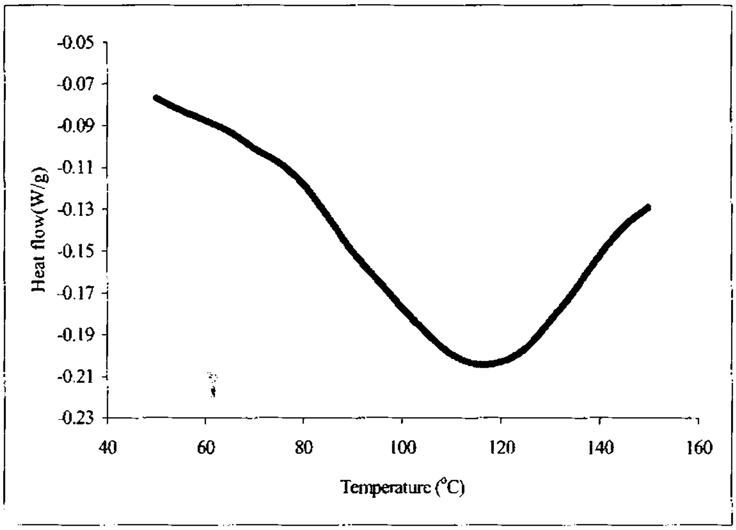


Figure 3.13: DSC thermogram of PAni [HClO$_4$]

[iii] Scanning electron microscopy [SEM]

The SEM photograph [Figure 3.14] of polyaniline shows that the chains are loosely packed and has a grain size of 1 µm.

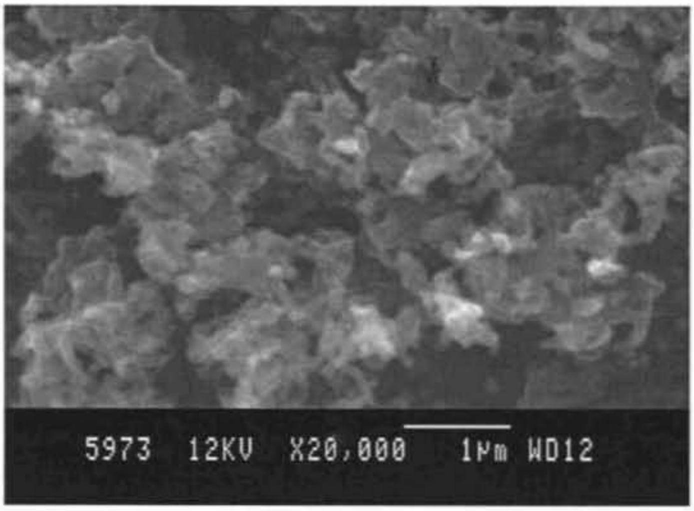


Figure 3.14: Scanning electron micrograph of PAni [$HClO_4$]

II Dielectric properties of $HClO_4$ doped Polyaniline

Among the inorganic dopants studied, the best dielectric behavior has been observed for $HClO_4$ doped samples. Since dielectric behavior of a material varies with the frequency of the electromagnetic wave. The variation of dielectric parameters in $HClO_4$ doped samples over the frequency range of 2 GHz - 4 GHz is described in this section.

1. Dielectric loss (ε'') and Conductivity (σ)

Figure 3.15 shows the variation of dielectric loss of $HClO_4$ doped PAni in pellet form with frequency. It is clear from the figure that the dielectric loss increases with frequency. The dielectric loss at S band is due to the free charge motion within the material as cited in the introduction [42,43].

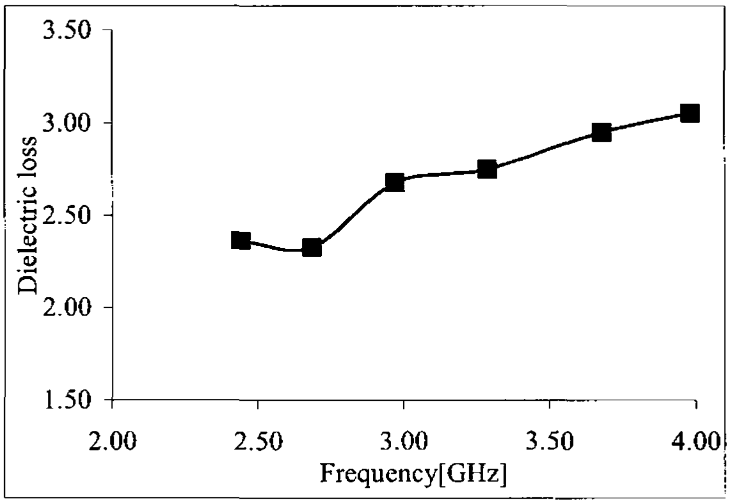


Figure 3.15: Variation of dielectric loss with frequency for $HClO_4$ doped samples

As the frequency is increased the inertia of the molecule and the binding forces become dominant and it is the basis for high dielectric loss at higher frequencies. The dielectric loss factor leads to so-called 'conductivity relaxation'. Figure 3.16 also shows the variation of conductivity of polyaniline with frequency. The real part of complex conductivity (ε') is generally considered as a.c conductivity as cited earlier[44] and it is often used to describe the frequency dependence of conductivity. The microwave conductivity is a direct function of dielectric loss and so it shows the same variation with frequency as the dielectric loss factor.

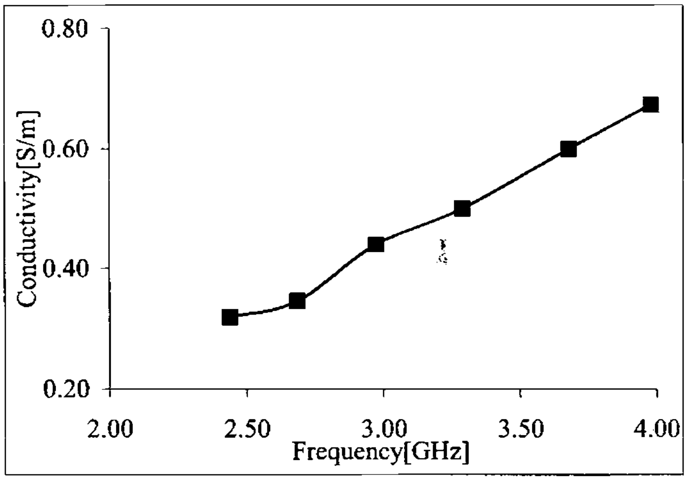


Figure 3.16: Variation of conductivity with frequency for $HClO_4$ doped samples

2. Dielectric constant (ε′)

The variation of real part of complex permittivity (dielectric constant) with frequency for Polyaniline samples is shown in Figure 3.17. The polarization in the microwave region is caused by the alternating accumulation of charges at interface due to the presence of dopants, leading to orientation polarization. When the frequency is increased, the rotational displacement of molecular dipoles under the influence of alternating field causes dielectric relaxation occurs and this may lead to a decrease in dielectric constant as observed earlier[38].

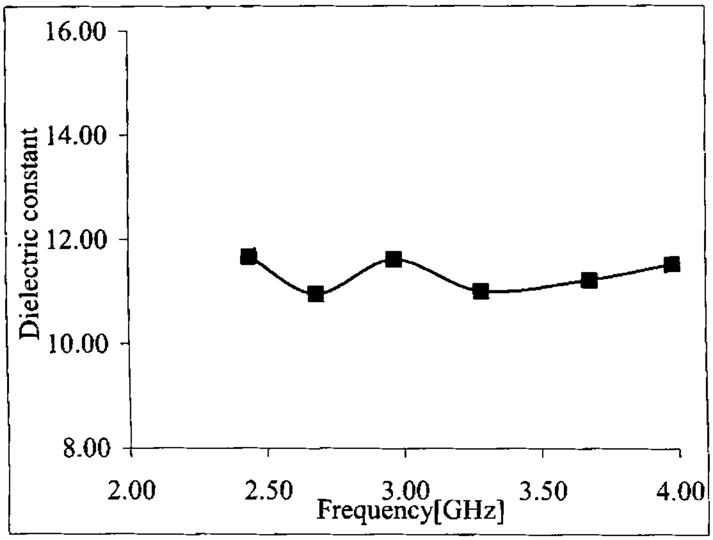


Figure 3.17: Variation of dielectric constant with frequency for $HClO_4$ doped samples

3. Loss Tangent (tan δ)

Figure 3.18 shows the variation of loss tangent of polyaniline samples with frequency. As the loss tangent is directly related to the dielectric loss it shows the same behaviour as that of dielectric loss.

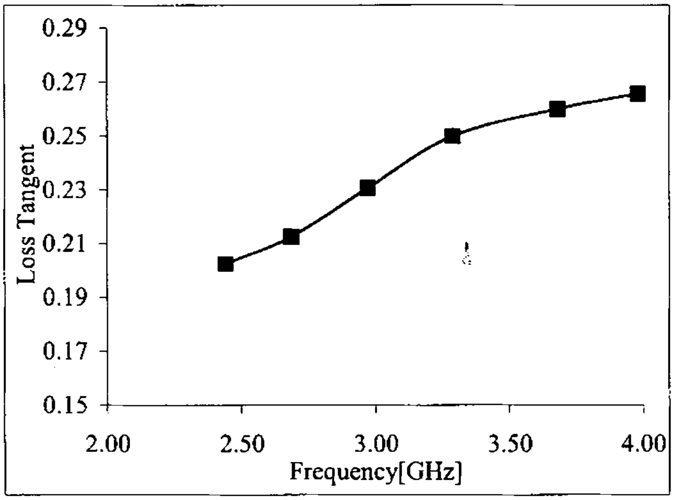


Figure 3.18: Variation of loss tangent with frequency for $HClO_4$ doped samples

4. Dielectric heating coefficient (J)

Figure 3.19 shows the variation of dielectric heating coefficient with frequency.

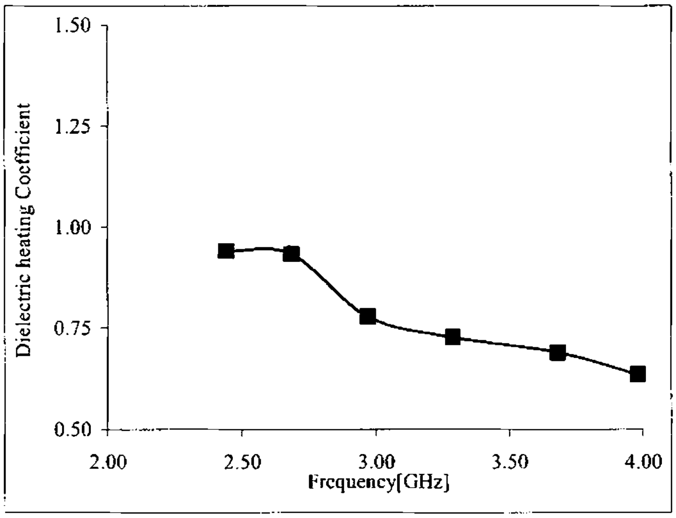


Figure 3.19: Variation of dielectric heating coefficient with frequency for $HClO_4$ doped samples

The heating coefficient is inversely related to the loss tangent and hence it decreases with increase in frequency.

5. Absorption coefficient and Penetration depth

Figure 3.20 shows the variation of absorption coefficient with frequency. The absorption coefficient is directly related to the dielectric loss factor and therefore it shows the same behaviour as dielectric loss. The variation of skin depth with frequency is given in Figure 3.21. It is clear from the figure that the skin depth decreases with increase in frequency. As the skin depth also called penetration depth, is basically the effective distance of penetration of an electromagnetic wave into the material for which the amplitude of the signal wave is reduced to 1/e or 37% of its maximum amplitude[45], it can be applied to a conductor carrying high frequency signals.

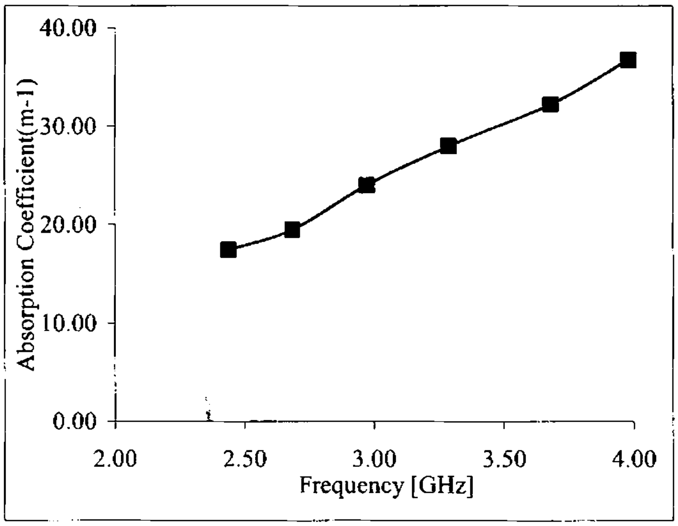


Figure 3.20: Variation of absorption coefficient with frequency for $HClO_4$ doped samples

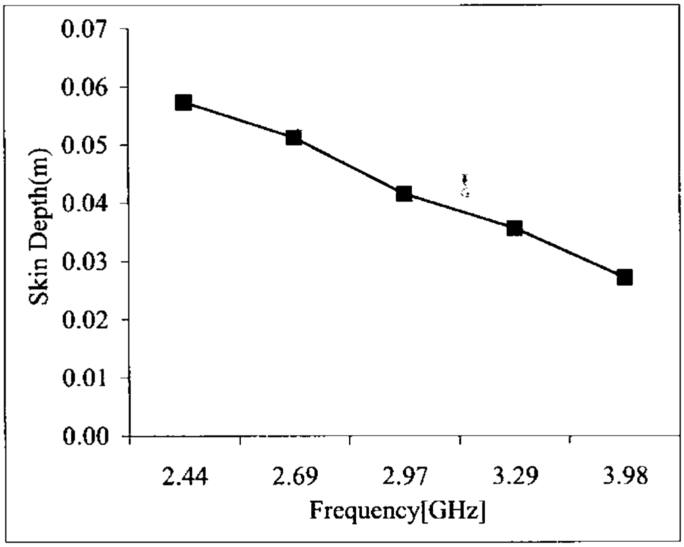


Figure 3.21: Variation of skin depth with frequency for $HClO_4$ doped samples

3.2.3.4 Effect of organic Dopants

1. Dielectric loss (ε″) and Conductivity (σ)

Figure 3.22 shows the dielectric loss and conductivity of Polyaniline in situ doped with organic sulphonic acids. The dielectric loss and conductivity of camphor sulphonic acid doped samples shows higher values compared to toluene sulphonic acid and naphthalene sulphonic acid doped samples. When a microwave field is applied to a polar material, the dipoles orient themselves with the field called dipolar polarization, leading to dielectric loss and conductivity. When the size of the chain is reduced, the chains are more flexible and therefore the dipole alignment on the application of a field becomes more rapid compared to longer chains[46]

The scanning electron micrographs of CSA (Figure 3.23a) and NSA (Figure 3.23b) doped samples show that CSA gives shorter chains of average grain size 1 µm compared to 10µm of NSA doped samples. This may be the reason why CSA give higher values of dielectric loss and conductivity than NSA, even though the sizes of counter ions are comparable. Another factor is that the CSA doped Polyaniline is the more solubilized form compared to the other dopants, which also contribute to higher dielectric loss for CSA doped Polyaniline owing to the greater flexibility of the chains.

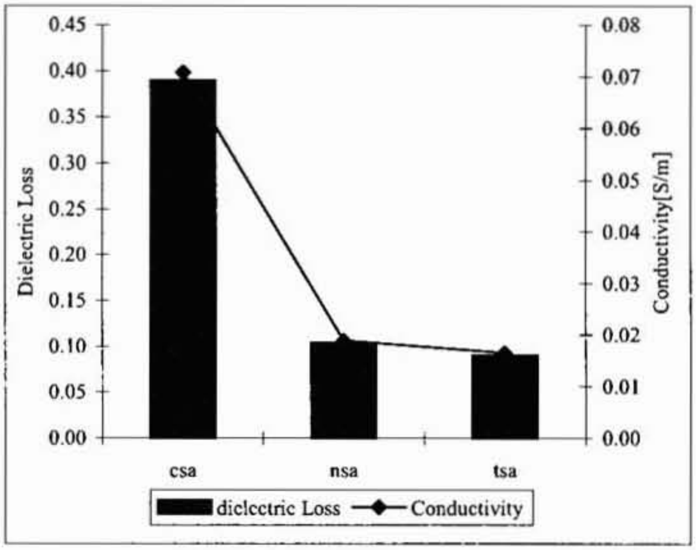


Figure 3.22: Effect of different organic sulphonic acids on the dielectric loss and conductivity of Polyaniline at 2.97 GHz

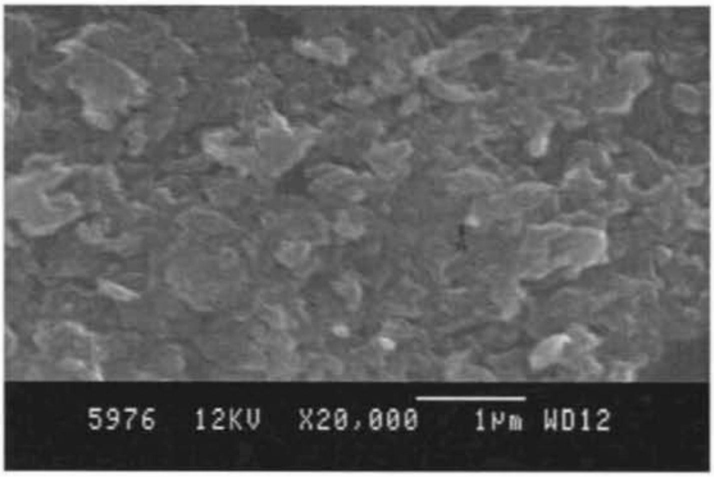


Figure 3.23a: Scanning electron micrograph of PAni [CSA]

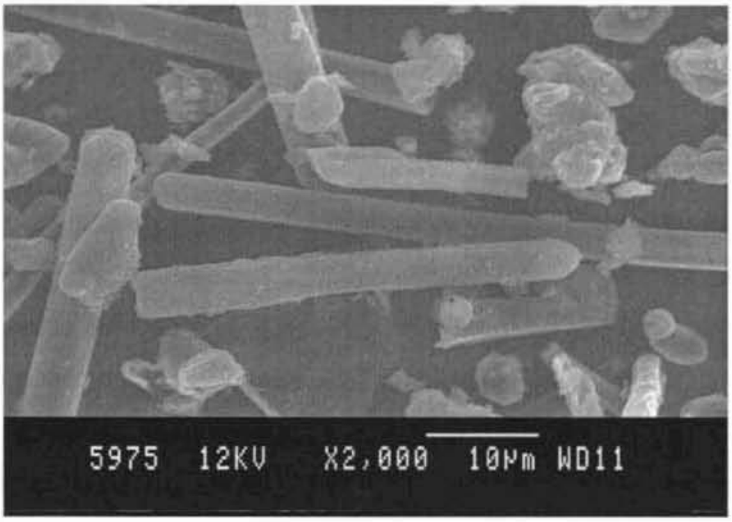


Figure 3.23 b : Scanning electron micrograph of PAni [NSA]

2. Dielectric constant (ε′) and Dielectric Heating Coefficient (J)

Figure 3.24 shows that the dielectric constant of CSA doped sample are higher compared to the other dopants. The shorter chain length of CSA doped polyaniline increases free charge motion that in turn increasing the capacitive coupling between the chains and thus increases the dielectric constant[46]. It is also clear from the figure that the dielectric heating coefficient is minimum for CSA doped samples as expected.

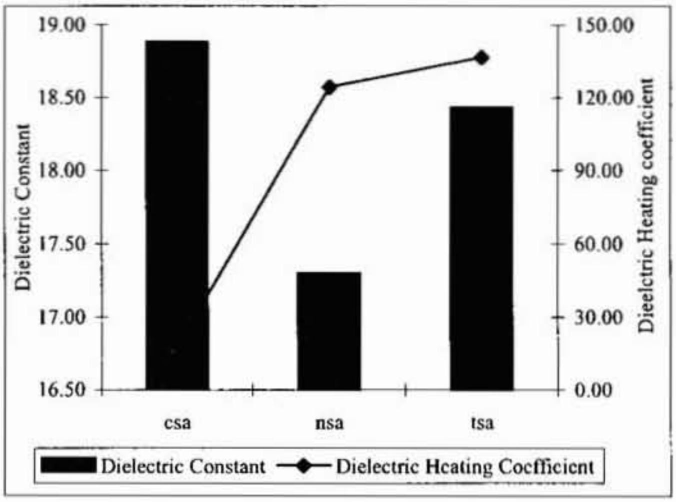


Figure 3.24: Effect of different organic sulphonic acids on the dielectric constant of Polyaniline at 2.97 GHz

3. Loss tangent (tan δ) and Absorption Coefficient

Figure 3.25 shows the variation of loss tangent and absorption coefficient of Polyaniline samples. Since the loss tangent and the absorption coefficient are directly related to the dielectric loss, they show a proportional behavior.

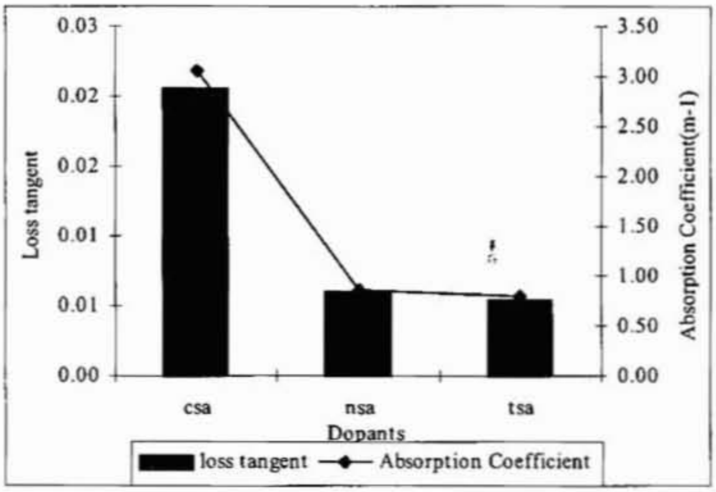


Figure 3.25: Effect of different organic sulphonic acids on the Loss tangent and absorption coefficient of Polyaniline at 2.97 GHz

3.2.2.5 Characterization and Dielectric Studies of Polyaniline without dopants [PAni undoped]

I.Characterisation

[i] IR spectroscopy

Figure 3.26 shows the IR spectrum of polyaniline prepared in the absence of dopants. The band at 3208 cm^{-1} indicates the -NH stretching vibration and the peaks at 1567 cm^{-1} and 1487 $cm^{-1}$and 802 cm^{-1} are due to the aromatic benzene ring structure in polyaniline. The spectral studies confirm the formation of polyaniline prepared in neutral medium as shown in the Figure 3. 26.

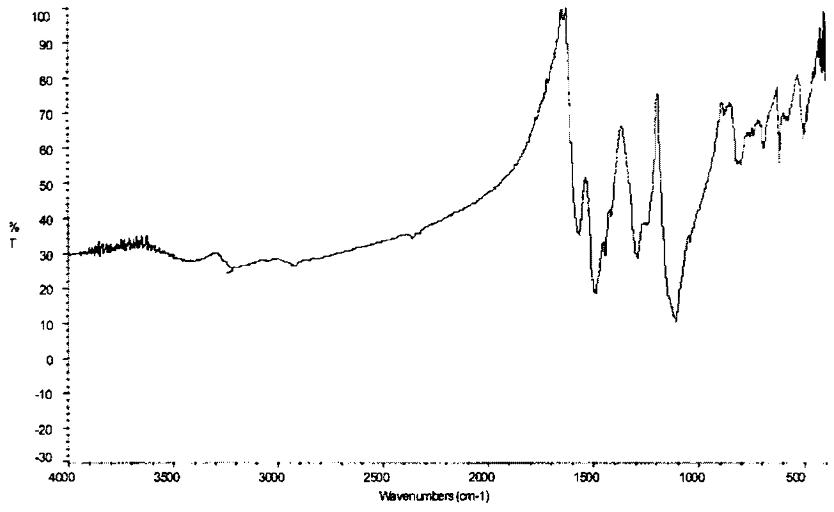


Figure 3.26: IR spectrum of undoped polyaniline

[ii] Thermal analysis

Figures 3.27 and 3.28 show the TGA and DSC thermogram of undoped Polyaniline samples. TG curve indicates a weight loss of 10% for polyaniline due to evolution of water at 130°C. Then the degradation of polyaniline chains starts at 130 °C and from 130°C to 550°C about 54% of weight loss indicate the degradation of polyaniline chain. Here the degradation of polyaniline chains starts much earlier than $HClO_4$ doped Polyaniline. Figure 3. 28 shows that the glass transition temperature (Tg) of polyaniline is 100°C.

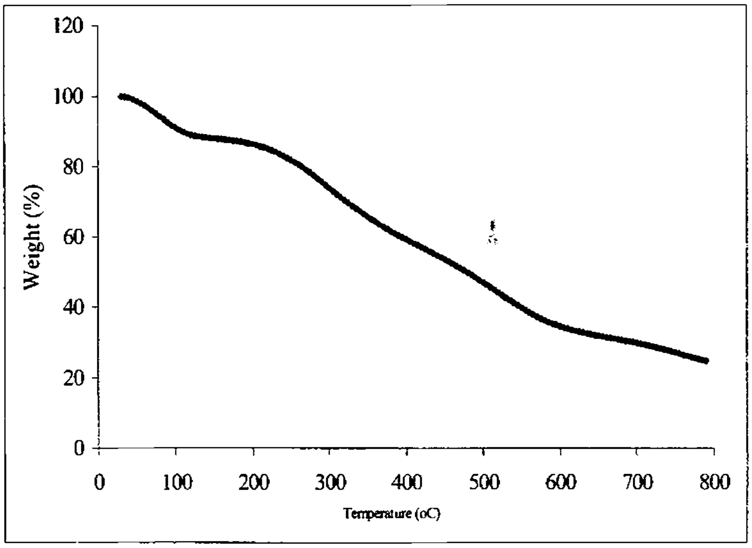


Figure 3.27: TGA thermogram of PAni [undoped]

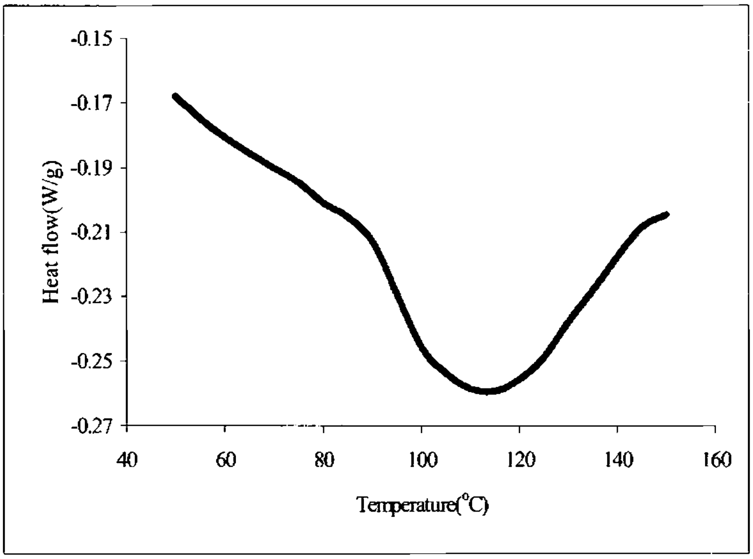


Figure 3.28: DSC thermogram of PAni [undoped]

iii Scanning Electron Microscopy

Scanning electron micrograph of undoped Polyaniline [Figure 3.29] shows that the chains are loosely packed and has a size of 1μm. It also shows that it is amorphous in nature.

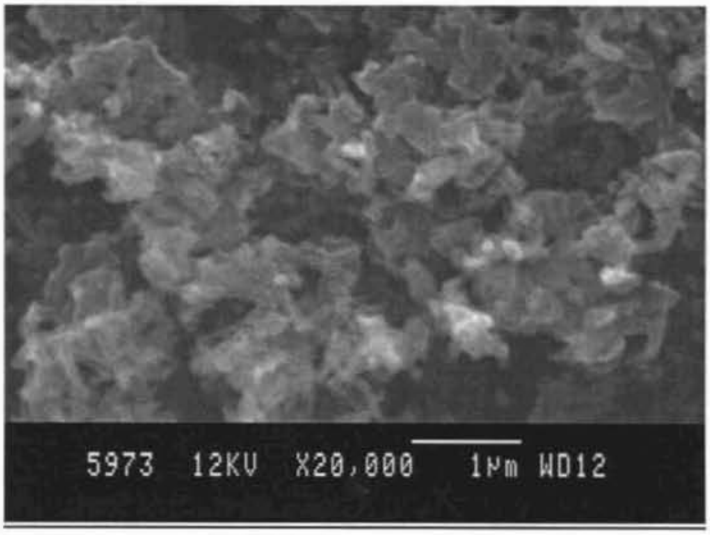


Figure 3.29: Scanning electron micrograph of undoped Polyaniline

II Effect of temperature on the dielectric properties of undoped Polyaniline

1.Dielectric loss (ε″) and Conductivity (σ)

Figure 3.30 shows the dielectric loss and conductivity of undoped Polyaniline prepared at 0-5 °C [LT], room temperature [RT] (28°C) and at high temperature [HT] (60°C) at a microwave frequency of 2.97 GHz. It is clear from the figure that the dielectric loss and conductivity are similar for Polyaniline prepared at low temperature and room temperature. The overall polarizability of a molecule is the sum of electronic, atomic and orientation polarization;

$\alpha_T=\alpha_e+\alpha_a+\alpha_o$. Undoped Polyaniline is non polar and in non polar materials the orientation polarization is absent and the polarizability arises from two effects; electronic and atomic polarization. This polarization's leads to dielectric loss and conductivity[47]. When the polymerization is carried out at a higher temperature, head to head sequence of polyaniline increases, thereby reducing the conjugation length of polyaniline, which in turn reduces the electronic polarization. Also the lower conjugation length leads to a decreased intrachain conduction and since the intrachain conduction is more compared to the interchain conduction, the high temperature prepared samples show less dielectric loss and conductivity. Since the conductivity in the microwave field is directly related to the dielectric loss factor, the conductivity is also higher for polyaniline prepared at room temperature and low temperature.

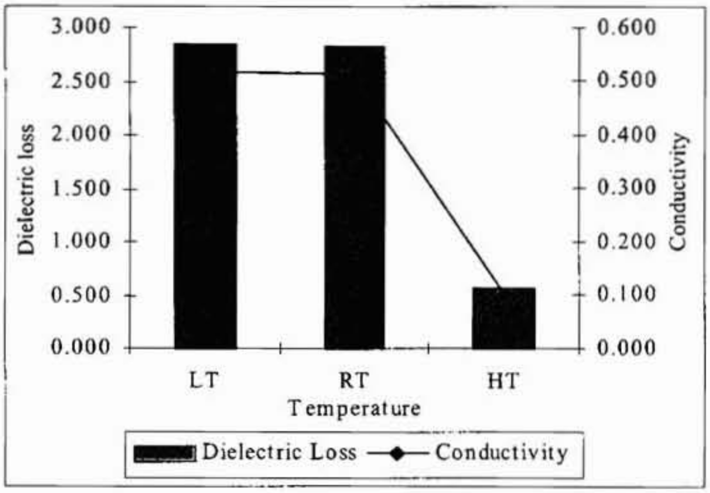


Figure 3.30: Effect of temperature on the dielectric loss and conductivity of undoped Polyaniline

2. Dielectric constant [ε′] and Dielectric Heating coefficient [J]

Figure 3.31 shows that the dielectric constant is high for undoped PAni prepared at low temperature. The capacitive coupling is high in the case of PAni prepared at low temperature and hence the dielectric constant is high for the same. The heating coefficient is a minimum for the room temperature prepared sample.

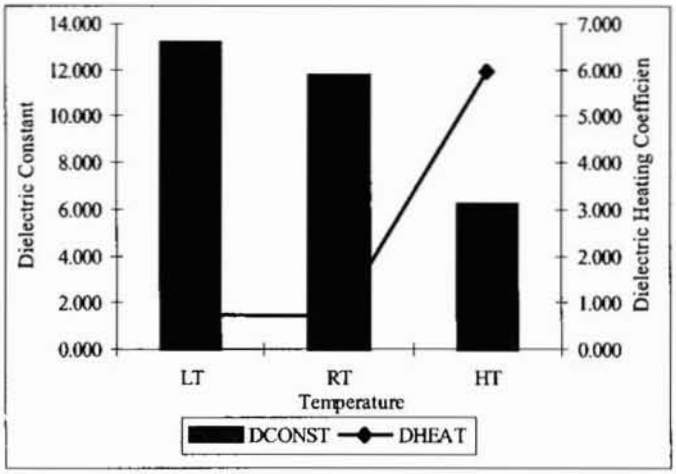


Figure 3.31: Effect of temperature on the dielectric constant and dielectric heating coefficient of undoped Polyaniline

4. Loss Tangent [tan δ] and Absorption coefficient

Figure 3.32 shows the variation of loss tangent and absorption coefficient of the undoped Polyaniline samples. It follows the same order as that of dielectric loss

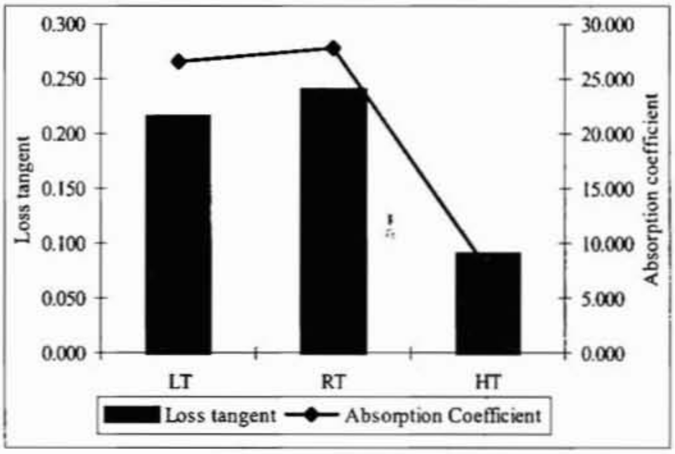


Figure 3.32: Effect of temperature on the Loss tangent and Absorption coefficient of undoped Polyaniline

4. Skin Depth

The penetration depth or skin depth is a measure of the suitability of a material for EMI shielding applications. The low temperature and room temperature samples can be used for shielding applications since the skin depth is a minimum for the low temperature and room temperature prepared samples as shown in Figure 3.33.

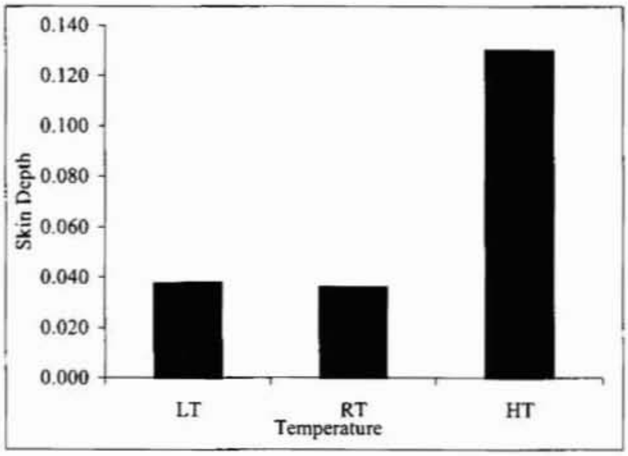


Figure 3.33: Effect of temperature on the Skin Depth of undoped Polyaniline

III Effect of frequency on the dielectric properties of undoped Polyaniline

Table 3.1: Variation of dielectric properties of undoped PAni with frequency

Property	Frequency (GHz)				
	2.44	**2.97**	**3.29**	**3.63**	**3.98**
Dielectric Loss (ε''_r)	3.462	4.561	3.943	4.508	4.640
Conductivity(σ S/m)	.468	.751	.846	.870	.906
Dielectric Constant (ε'_r)	13.89	13.62	12.77	12.67	12.55
Dielectric Heating Coefficient (J)	.579	.379	.358	.372	.452
Loss Tangent (tan δ)	.249	.335	.363	.356	.314
Absorption Coefficient (m^{-1})	23.30	37.32	43.20	46.52	45.17
Skin Depth (m)	.043	.027	.023	.021	.022

Table 3.1 shows the variation of the dielectric properties of undoped PAni with change in frequency. It also shows the same behavior as that of doped polyaniline samples. In the case of undoped samples the dielectric loss, conductivity, loss tangent and absorption coefficient are found to increase with frequency while dielectric constant, penetration depth and dielectric heating coefficient decrease with frequency.

3.2.2.6 Comparison of the Dielectric Properties of PAni[Undoped], PAni[$HClO_4$] and PAni[CSA]

Table 3.2: Comparison of dielectric properties of PAni[undoped], PAni[HClO4], PAni[CSA]

Dielectric property	**PAni [Undoped]**	**PAni [HClO4]**	**PAni [CSA]**
Dielectric Loss (ε''_r)	**4.5**	2.68	0.3
Conductivity(σ S/m)	**0.75**	0.44	0.05
Dielectric Constant(ε'_r)	**13.63**	11.60	18
Dielectric Heating Coefficient (J)	**0.38**	0.78	26.03
Loss Tangent (tan δ)	**0.33**	0.23	0.02
Absorption Coefficient (m^{-1})	**37.33**	24.02	2.18
Skin Depth (m)	**0.03**	0.04	0.46

The dielectric parameters of PAni [undoped], PAni [HClO4], and PAni [CSA] are compared in Table 3.2. It is clear from the table that the dielectric properties of undoped Polyaniline are superior than CSA doped and $HClO_4$ doped Polyaniline. In the case of undoped Polyaniline, when the microwave is passed through the material, electronic polarization takes place, which will increase the intrachain conduction. Polyaniline prepared in the undoped state contains more head to head aligned segments compared to the doped state. In such cases, the dielectric constant and conductivity of two regions within the same matrix (head to head alignment and head to tail alignment) are different or heterogeneous in nature. This difference in the dielectric constant and conductivity at different regions of Polyaniline chain leads to interfacial polarization which enhances the dielectric loss and conductivity[48]. In the case of $HClO_4$ dopant, the size is less and the doping is not diffusion limited, when compared to CSA dopant and hence the former shows better relaxation leading to high dielectric loss. Since the conductivity is directly related to the dielectric loss factor the conductivity is also higher for $HClO_4$doped samples compared to CSA samples.

When the size of the dopants are high, the interchain distance between the polymer chains increases, which results in a decreased capacitive couplings and hence the low values of dielectric constant as noted earlier[49] for CSA doped Polyaniline samples.

Dielectric heating coefficient is least for undoped sample. The dielectric heating coefficient is inversely related to the dielectric loss factor and hence the undoped samples show the minimum value. The loss tangent and absorption coefficient are higher for undoped polyaniline and penetration depth or skin depth is low for undoped polyaniline, as expected.

PART II

3.3: STUDIES ON POLY o-TOLUIDINE AND POLY o-ANISIDINE

3.3.1: INTRODUCTION

A number of conducting polymers have been extensively studied in the last decades, in particular because of the great possibilities of application they offer such as electronic and optical devices, and batteries[50,51]. Polyaniline (PAni) is by far the most investigated conducting polymer, and it can be usually synthesized by chemical or electrochemical oxidation of aniline in aqueous and non-aqueous media[52]. The main difference between these two methodologies of synthesis is that the electro polymerization of aniline allows one to obtain details on the processes of charge transfer of a film directly deposited on an electrode surface. The chemical polymerization of aniline in the presence of a strong oxidizing agent is suitable when a large quantity of a powdery material is required. The disadvantage of the chemical oxidation techniques is that chemically synthesized PAni exhibits limited solubility in most common organic solvents, making it more difficult to cast films out of it. As a result, substituted PAni's[53-56]] have been synthesized in order to improve solubility of this class of polymers. However, most of these derivatives exhibit characteristically low values of molecular weight and electric conductivity.

Many papers have been published on the progress of the electrochemical and chemical polymerization of aniline and derivatives in order to correlate mechanisms of oxidation of aniline and properties of PAni such as electrical conductivity, molecular weight, and crystallinity[53-59]. However, these works have been mainly focussed in the kinetics of electrochemical polymerization of aniline, in which the rate-limiting step has been attributed to the formation of radical cations[57-59].

Poly (*o*-toluidine) (PoT) and poly *o*-anisidine(PoAn) are the methyl and methoxy derivative of the extensively studied polyaniline system [[60]]. Like the parent material, electroactive PoT films are readily prepared and are stable in aqueous acid media. Electrochemically-driven film redox switching requires exchange of ions with the bathing electrolyte to maintain film electroneutrality. For most electroactive polymer films, ion (rather than electron) transport is rate limiting. For PoT films in aqueous acid solutions, one can envisage circumstances in which electroneutrality may be satisfied by balanced transfers of electrons and protons. This offers huge advantages from an applications viewpoint, since protons transfer an order of magnitude faster than most other ions. Gupta et al have reported that the thermal stability of doped poly [*o*-anisidine] strongly depends upon counterions.

The aim of this study is to investigate the chemical oxidative synthesis of the Polyaniline derivatives poly[o-toluidiene] and poly[o-anisidine] in presence of various dopants and to focuse on the dielectric properties of these materials in the microwave field of 2-4 GHz which holds relevance for Industrial, Scientific and Medical [ISM] applications. Although different authors have already reported results on the electrical and optical properties of Poly[o-toluidine], in particular as blends and fibres[61-63] very sparse literature is found on the dielectric behavior of this Polyaniline derivative in the microwave field. Hence the behavior of the analogues of Polyaniline are also proposed to be investigated in the microwave field

3.3.2 EXPERIMENTAL

- ***Preparation of Poly o-toluidine & Poly o-Anisidine [Doped form -In situ polymerisation]***

With inorganic dopants: Chemical oxidative polymerisation of o-toluidine and o-Anisidine to give the conducting form was carried out using ammonium persulphate as initiator in the presence of 1M HCl at 0-5 ^{0} C [LT], room temperature [RT] and at 60°C [HT]. The reaction was carried out for 4 hrs. The precipitate formed was filtered and was washed with water, acetone and methanol. The samples were then oven dried at 50- 60 ^{0}C for 6h. The reaction was repeated with 1M solutions of different dopants like sulphuric acid, nitric acid and perchloric acid. The undoped form of PoT and PoAn was prepared by the same procedure as outlined, but in the absence of any inorganic acids.

3.3.3 RESULTS AND DISCUSSION:

3.3.3.1 Effect of Different Inorganic Dopants on the Dielectric Properties of Poly o-Toluidine And Poly o-Anisidine:

As explained in the first section of the chapter the undoped and $HClO_4$ doped PAni show better response in the microwave field among the other samples. Based on these results, the conditions have further been narrowed down to understand the dielectric response of Poly o-toluidine and Poly o-Anisidine. The methoxy derivative of Polyaniline, Poly [o-anisidine] has been studied for various inorganic dopants.

1. Dielectric loss (ε″) and Conductivity (σ):

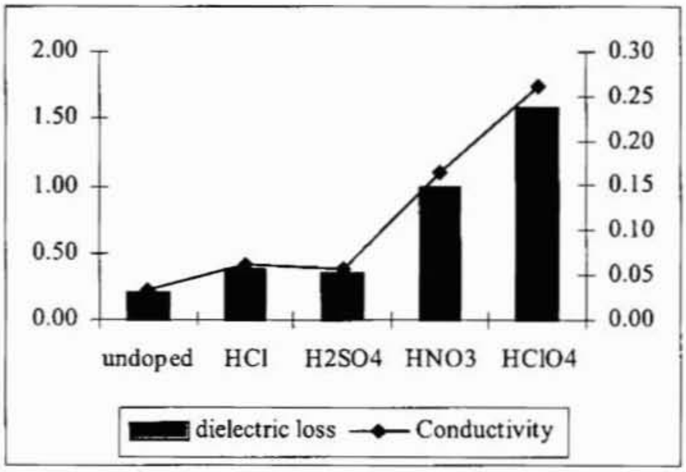


Figure 3.34: Effect of dopants on the dielectric loss and conductivity of PoT

Figures 3.34 and 3.35 show the variation of dielectric loss and conductivity of PoT and PoAn respectively. It may be observed that the dielectric loss and conductivity of $HClO_4$ doped PoT are higher than those of polyaniline.

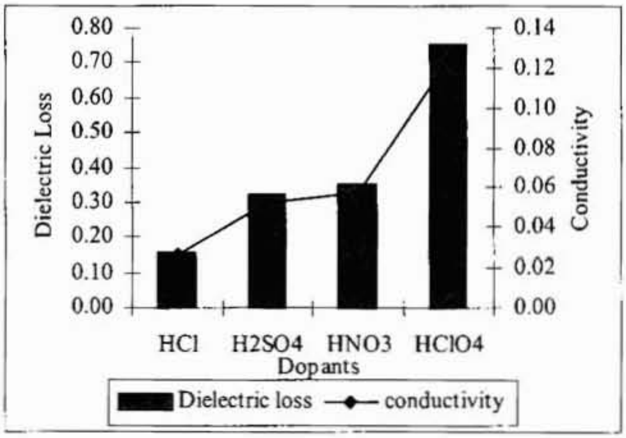


Figure 3.35: Effect of dopants on the dielectric loss and conductivity of PoAn

Here the undoped samples show minimum values. The introduction of a substituent group (-CH_3 group in *o*-toluidine and the -OCH_3 group in o-anisidine) increases the torsional angle between the two adjacent phenylene rings and facilitates better solvation at the -NH group on the polymer backbone. This would lead to reduced conjugation of the polymer and hence reduced conductivity[61]. Since the electronic polarization plays the key factor in increasing the microwave conductivity, the reduction in conjugation length will reduce the conductivity of the undoped state.

2. Dielectric Constant (ε')

Due to the polarization of dielectric materials the accumulation of charges at the interphase between different phases of the material takes place which results in dielectric constant. In PoT and PoAn samples the dielectric constant for $HClO_4$ dopant is high [Figure 3.36 and 3.37] as in the case of PAni samples.

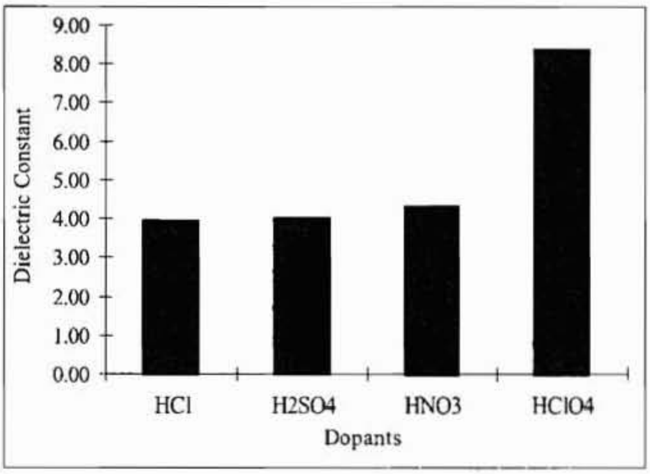


Figure 3.36: Effect of dopants on the dielectric constant of PoT

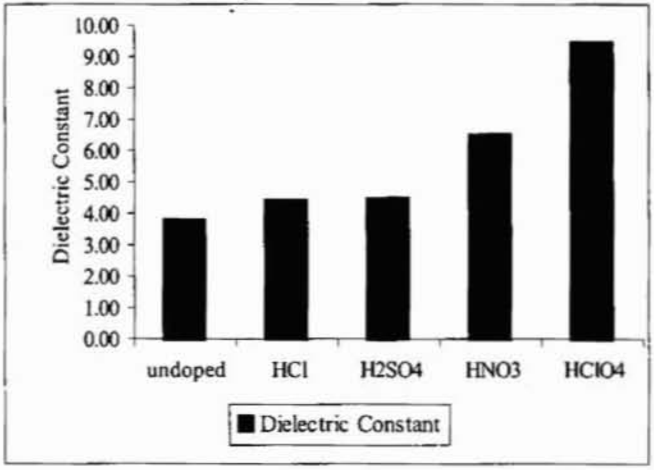


Figure 3.37: Effect of dopants on the dielectric constant of PoAn

3. Dielectric heating coefficient and Loss tangent

Figures 3.38 and 3.39 show that the loss tangent is high and the dielectric heating coefficient is a minimum for HClO4 doped samples .The reason for this behaviour is same as explained in the case of polyaniline.

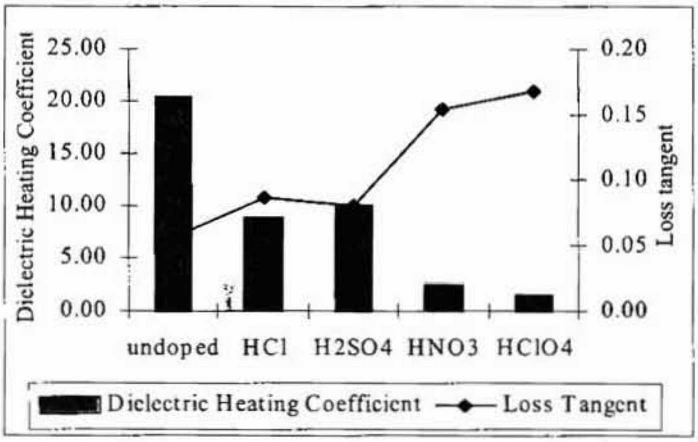


Figure 3.38: Effect of dopants on the dielectric heating coefficient and Loss tangent of PoT

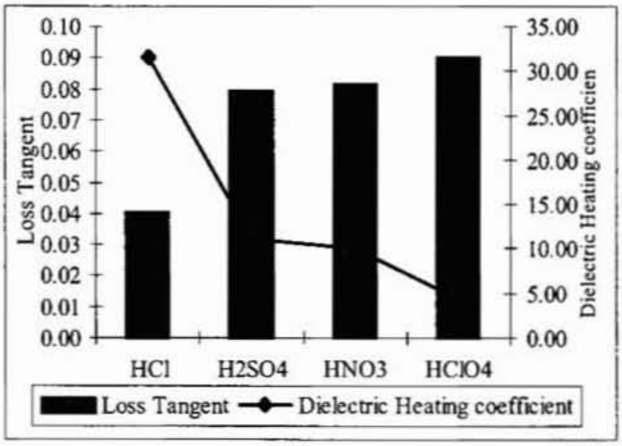


Figure 3.39: Effect of dopants on the dielectric heating coefficient and Loss tangent of PoAn

4. Absorption Coefficient and Skin Depth

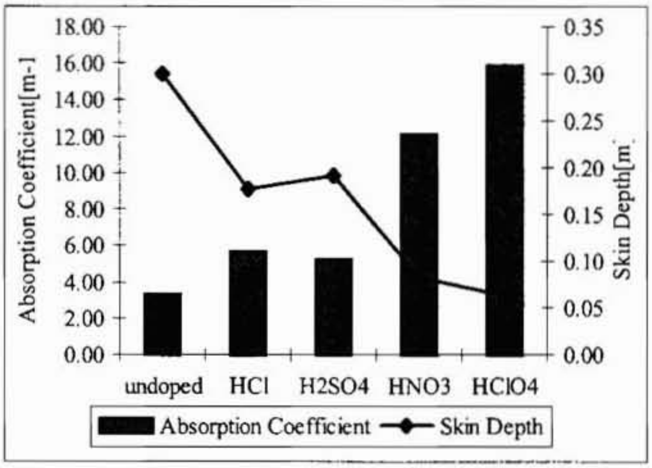


Figure 3.40:Effect of dopants on the Absorption coefficient and Skin depth of PoT

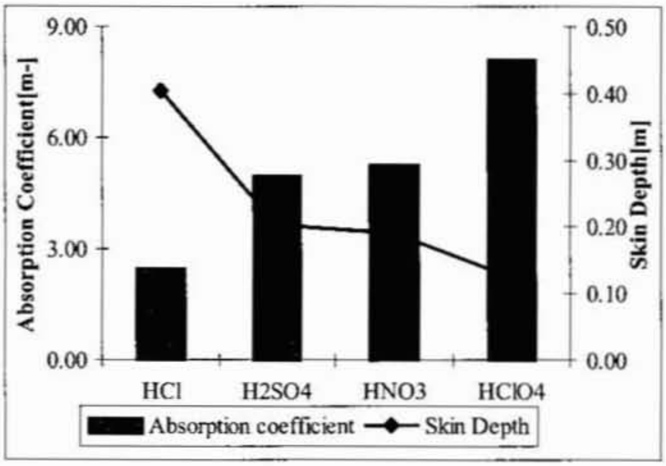


Figure 3.41: Effect of dopants on the Absorption coefficient and Skin depth of PoAn

It is evident from the figure 3.40 and 3.41 that the absorption coefficient is high and skin depth is a minimum for $HClO_4$ doped samples compared to all other samples, as expected.

The variation of dielectric properties with frequency of $HClO_4$ doped samples of PoT and PoAn follows a similar trend as the PAni $HClO_4$ doped samples. A typical graph of conductivity of pellet samples of PoT and PoAn with frequency is shown in the figure 3.42.

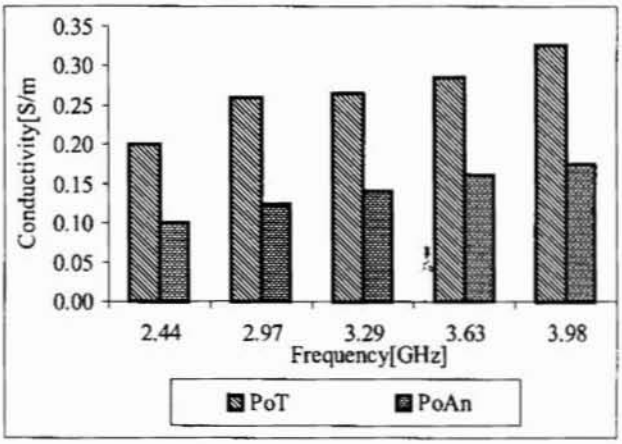


Figure 3.42: Variation in conductivity with frequency of PoT and PoAn

3.4 COMPARISON BETWEEN MATRICES

Table 3.3 shows a comparison of the dielectric properties of matrices such as PAni [$HClO_4$], PoT [$HClO_4$], PoAn[$HClO_4$]. The dipole developed in polyaniline due to the protonation, ($-NH^+ClO_4^-$)and hence is more free to undergo rotational displacement in an a.c. field when compared to other polymers. In the case of poly o-toluidine, the presence of $-CH_3$ group develops sterric hindrance and it may adversely affect the rate of dipole change. In the case of poly o-anisidine, the -OCH3 group is more bulky than -CH3 in PoT and hence the steric hindrance is more pronounced in PoAn. It is clear from the data that the PAni [$HClO_4$] shows highest dielectric loss and conductivity. The dielectric constant of polyaniline samples is high compared to PoT and PoAn samples. Since the dielectric constant is dependent upon the accumulation of polar charges at the interface of the molecule a higher value for polyaniline is expected when compared to that of others. In the case of PoT and PoAn the accumulation may be less because of the presence of $-CH_3$ and $-OCH_3$ group. The dielectric heating coefficient is defined as $J = 1/\varepsilon_r \tan \delta$. The loss tangent tan δ is directly related to the dielectric loss and inversely related to the dielectric constant and therefore the heating coefficient is strongly dependent on these factors. The lower the J value the better will be the material for dielectric heating applications and the polyaniline samples show minimum for dielectric heating coefficient.

Table 3.3: Comparison of matrices.

Dielectric property	**PAni[$HClO_4$]**	**PoT[$HClO_4$]**	**PoAn[$HClO_4$]**
Dielectric Loss (ε''_r)	2.68	1.58	.75
Conductivity (σ S/m)	.44	.26	.12
Dielectric Constant (ε'_r)	11.6	9.43	8.35
Dielectric Heating Coefficient J	.78	1.54	4.41
Loss Tangent (tan δ)	.23	.17	.09
Absorption Coefficient(m^{-1})	24.02	15.88	8.08
Skin Depth (m)	.04	.06	.12

Polyaniline shows a high dielectric loss and hence high absorption coefficient as shown in the table. The skin depth of polyaniline is lower when compared to other polymers. It is very important to study the absorption coefficient and penetration depth for applications like electro magnetic interference (EMI) shielding. The absorption coefficient is dependent on the dielectric loss factor and is inversely related to the refractive index. For highly lossy materials the absorption coefficient is very high and the skin depth (the factor indicating the penetration of wave in to material) is minimum

PART III

3.5 DIELECTRIC RESPONSE OF SELECTED CONDUCTING MATRICES IN THE HIGH FREQUENCY FIELD

3.5.1: EFFECT OF INORGANIC DOPANTS:

Figure 3.43,3.44 and 3.45 shows the dielectric constant, loss tangent and conductivity of polyaniline prepared with inorganic dopants at room temperature, respectively.

The large positive value of permittivity has been found at room temperature. This may be due to the large effective size of metallic islands and easy charge transfer through well ordered polymer chains in disordered regions as suggested by Joo et al[64]. The high dielectric constant at low frequency is linked to the heterogeneity of materials (conductivity variation along the conducting paths)[65]. At high frequencies, ε' is relatively constant while at low frequencies ε' increases representing additional contributions to the dielectric response with an almost Debye-like relaxation mechanism[66].

In the low frequency range the conductivity is constant and equal to σ_{dc} and beyond a frequency the a.c. conductivity appears and then it will shows a linear relation ship with frequency. At low frequencies the charge conduction is due to the interaction between the charges among the different chains [67].

It is clear from the figure 3.44 that the loss tangent is decreased at first and then remains constant.

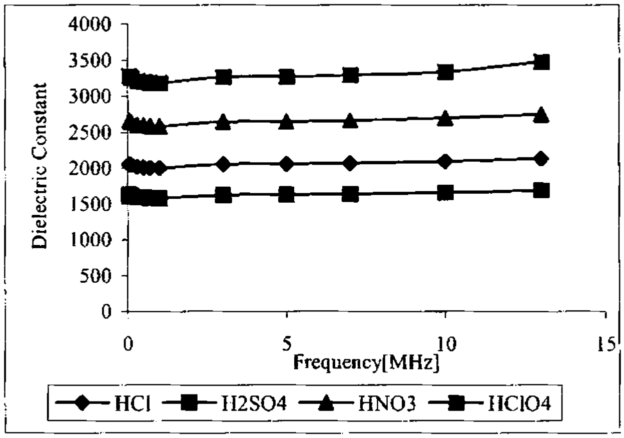


Figure 3.43: Effect of inorganic dopants on the dielectric constant of PAni

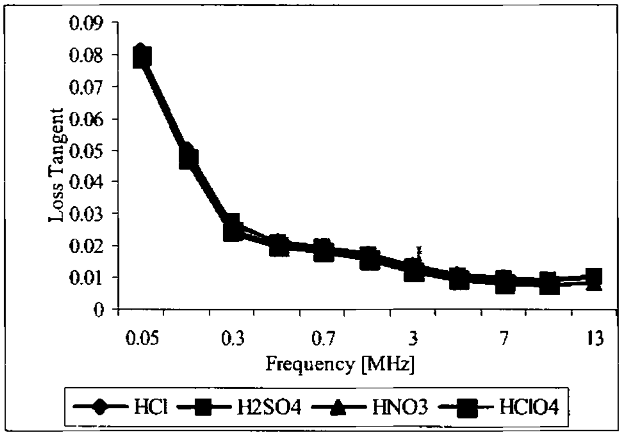


Figure 3.44: Effect of inorganic dopants on the loss tangent of PAni

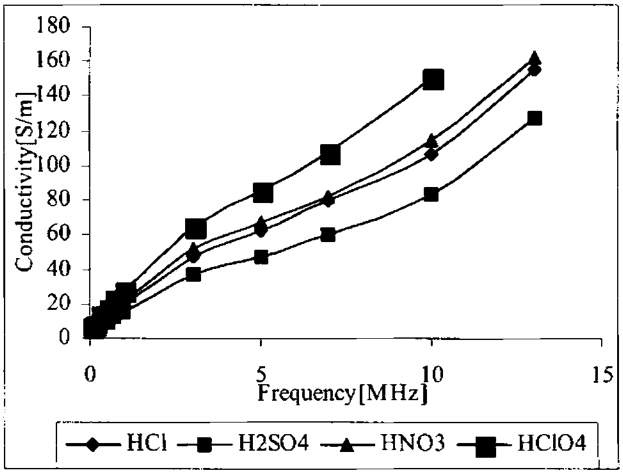


Figure 3.45: Effect of inorganic dopants on the conductivity of PAni

The figures also show that the dielectric constant and conductivity are higher for HclO4 doped samples.

3.5.2: EFFECT OF ORGANIC DOPANTS

Figures 3.46, 3.47 and 3.48 shows the, loss tangent, dielectric constant and conductivity of polyaniline prepared with organic dopants. It also shows the same behaviour with frequency as in the case of inorganic dopants. Also the CSA doped samples shows higher dielectric constant and conductivity compared to TSA and NSA dopants.

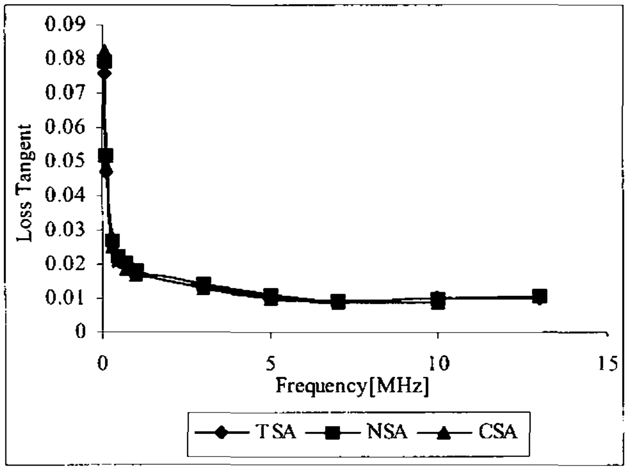


Figure 3.46: Effect of organic dopants on the loss tangent of PAni

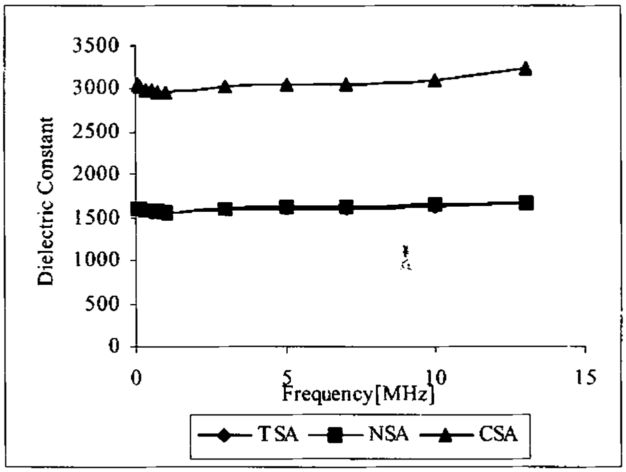


Figure 3.47: Effect of organic dopants on the dielectric constant of PAni

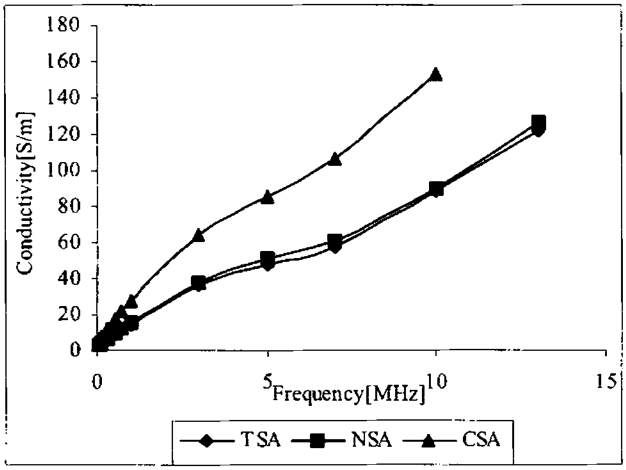


Figure 3.48: Effect of organic dopants on the conductivity of PAni

3.6 CONCLUSIONS

- ⇨ The polyaniline prepared at room temperature shows better microwave response compared to those prepared at low and high temperatures
- ⇨ The microwave response of $HClO_4$ doped PAni is better when compared to other inorganic dopants like HCl, HNO_3, H_2SO_4
- ⇨ The dielectric heating coefficient is a minimum for $HClO_4$ doped PAni and the conductivity is a maximum
- ⇨ The dielectric parameters such as loss, conductivity, loss tangent and absorption coefficient, all show a strong frequency dependence
- ⇨ Among the organic dopants, sulphonic acids like CSA, NSA, and TSA were efficient for in situ doping reaction. CSA doped samples showed better properties.
- ⇨ NSA imparted a tubular morphology to the PAni formed. This effect was not prevalent with the other acids used.
- ⇨ The undoped form of PAni prepared at room temperature and low temperature showed better properties when compared to high temperature prepared samples.
- ⇨ Among the three matrices namely PAni[HClO4], PAni[CSA] and PAni[undoped] , the undoped showed better conductivity, loss , loss tangent and absorption coefficient
- ⇨ The dielectric constant was found to be highest for the CSA doped Polyaniline sample.The methyl and methoxy derivative, Poly o-toluidine and Poly o- anisidine show better property when $HClO_4$ is used as dopant for the in situ reaction.

3.7 REFERENCES

1. C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, A.G. *MacDiarmid. Phys. Rev. Lett. 39, 1098–1101, (1977).*
2. J. H. Burroughes, C. A. Jones, R. H. Friend. *Nature* **335,** 137-141 (1988).
3. F. Garnier, R. Hajlaoui, A. Yassar, P. Srivastava. *Science* **265,** 1684–1686 (1994).
4. L. Torsi, A. Dodabalapur, L. J. Rothberg, A. W. P. Fung, H. E. Katz. *Science* **272,** 1462–1464 (1996).
5. A. R. Brown, A. Pomp, C. M. Hart, D. M. Deleeuw. *Science* **270,** 972–974 (1995).
6. G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger. *Science* **270,** 1789–1791 (1995).
7. J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B.Holmes. *Nature* **376,** 498–500 (1995).
8. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L.Burn, A. B. Holmes. *Nature* **347,** 539–541 (1990).
9. D. Braun and A. J. Heeger. *Appl. Phys. Lett.* **58,** 1982–1984 (1991).
10. N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, A. B. Holmes. *Nature* **365,** 628–630 (1993).
11. A. Kraft, A. C. Grimsdale, A. B. Holmes. *Angew. Chem. - Int. Ed. In Engl.* **37,** 402–428 (1998).

12. R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C.Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, W. R. Salaneck. *Nature* **397,** 121-127 (1999).
13. J. Salbeck. *Ber. Bunsenges. Phys. Chem.* **100,** 1667-1677 (1996).
14. R. H. Friend *Pure Appl. Chem.*, Vol. 73, No. 3, pp. 425-430, 2001
15. MacDiarmid, A. G., Chiang, J. C., Richter, A. F., Somasiri, N. L. D. and Epstein, A. J., in *Conducting Polymers*, ed. L. Alcacer. Reidel Publishing Co., Dordrecht, 1987, pp. 105-120.
16. MacDiarmid, A. G. and Epstein, A. J., *Faraday Discuss. Chem. Soc.*, 1989, **88,** 317-332.
17. Genies, E. M., Bogly, A., Lapkowsky, M. and Tsintavis, C., *Synth. Met.*, 1990, **36,** 139-182.
18. Yang, R. Cz. Ch., in *Large-area Chromogenics; Materials and Devices for Transmittance Control*, ed. C. M. Lampert and C. G. Granqvist. SPIE Optical Engineering Press, Bellingham, Washington, 1990, pp. 335-365.
19. MacDiarmid, A. G. and Epstein, A. J., *Macromol. Chem., Macromol. Symp.*, 1991, **51,** 11-28.
20. MacDiarmid, A. G., in Conjugated Polymers and Related Materials: the Interconnection of*Chemical and Electronic Structure*, ed. W. R. Salaneck and I. Lundstrom. Oxford Scientific Press, 1992.
21. MacDiarmid, A. G. and Epstein, A.J., in Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics, ed. J. L. Bredas and R. R. Chance.

22. Kluwer Academic, 1990.Travers, J.-P., Genoud, F., Menardo, C. and Nechtschein, M., *Synth. Met.*, 1990, **35**, 159-168.

23. Lux, F., *Polymer*, 1994, **35**, 2915-2936.

24. Epstein, A. J. and MacDiarmid, A., *Synth. Met.*, 1995, **69**, 179-182. and references therein.

25. Joo, J., Oh, E. J., Min, G., Epstein, A. J. and MacDiarmid, A., *Synth. Met.*, 1995, **69**, 251-254.

26. Epstein, A. J., Joo, J., Kohlman, R. S., Du, G., MacDiarmid, A., Oh, E. J., Min, Y., Tsukamoto, J.,Kaneko, H. and Pouget, J. P., *Synth. Met.*, 1994, 65, 149-157.

27. Trivedi, D. C. and Dhawan, S. K., *Synth. Met.*, 1993, 59, 267-272.

28. Huang, J.-Ch., *Adv. Polym. Technol.*, 1995, **14**, 137-150.

29. Joo, J. and Epstein, A. J., *Appl. Phys. Lett.*, 1994, **65**, 2278-2280.

30. Colaneri, N. F. and Shacklette, L. W., IEEE Transactions on Instrumentation and Measurements,1992, **41**, 291-297.

31. Hourquebie, P. and Olmedo, L., *Synth. Met.*, 1994, **65**, 19-26.

32. Olmedo, L., Hourquebie, P. and Jousse, F., *Synth. Met.*,1995, **69**,205-208.

33. Matveeva, E. S., Diaz Calleja, R. and Sanchez-Martinez, E., *Synth. Met.*, 1994, **67**, 207-210.

34. Diaz Calleja, R., Matveeva, E. S. and Parkhutik, V. P., *J. Non-Cryst. Solids*, 1995, **180**, 260-265.

35. Matveeva, E. S., Diaz Calleja, R. and Parkhutik, V. P., *Synth. Met.*, 1995, **72,** 105–110.

36. P.debye, Polar molecules, chemical catalog Co., New York (1929)

37. J.G. Kirkwood and R.M.Fuoss, J.chem. phys., **9**,329,1941

38. Stephen, C. W., Frederic, H. L., *"Microwaves made simple: principles and applications"* United States Bookcrafters, Chelsea, 1985.

39. R.J.Maccallum, C.A. Vincent, Polymer Electrolyte Reviews II, Elsevier Applied Science Publuishers Ltd, London and New York, 1987,Ch.2

40. Andreatta, A. J. Heeger and P. Smith, Polym. Communn. (1990), **31**, 275.

41. T.A. Ezquerra, F. Kremmer, G. Wegner AC, Dielectric properties of heterogeneous materials: Progress in Electromagnetic research, vol 6, Elsevier, New York, [1992]

42. K.L Ngai. R.W. Rendell,. *'Dielectric and Conductivity Relaxations in Conducting Polymers"* In: *Hand Book of Conducting Polymers,* Skotheim, T.A. (Ed.), Marcel Decker, New York, 1986.

43. V.Saravanan, S. Palaniappan,S. Seetharamu, Macromolecules New Frontiers, **1**, 344, (1995)

44. Jayashree Anand, Palle Swapna Rao, S. Palaniappan and D. N. Sathyanarayana, Macromolecules New Frontiers, **1**, 374, (1998)

45. Andreatta, A. J. Heeger and P. Smith, Polym. Communn. (1990), **31**, 275.

46. H.S.Nalwa Handbook of organic conductive Molecules and Polymer 1997 :Vol 3 chapter 8
47. C.Ku Chen and Raimong Liepins, Electrical properties of polymers, Hanser publications 1987, New York
48. J.C.Maxwell, Electricity and Magnetism, Oxford University press, oxford[1892]
49. J.G. Kirkwood and R.M.Fuoss, J.chem. phys., 9,329,1941
50. MacDiarmid AG. Sintetic metals: *Angewandte Chemie-International Edition.* 2001; 40(14):2581-90.
51. Kvarnström C, Ivaska A. *Handbook of Organic Conductive Molecules.* Nalwa HS ed; 1997.
52. Mattoso LHC.. *Química Nova.* 1996; 19(4):388-99.
53. Gonçalves D, dos Santos DS, Mattoso LHC, Karasz FE, Akcelrud L, Faria RM.. *Synth Metals.* 1997; 90(1):5-11.
54. Mattoso LHC, Faria RM, Bulhões LOS, MacDiarmid AG. *J Polymer Science Part A - Polymer Chem.* 1994; 32(11):2147-53.
55. Cattarin S, Doubova L, Mengoli G, Zotti G *Electrochimica Acta.*1988; 38(8):1077-84.
56. Wei Y, Sun Y, Tang J.. *J Phys Chem.* 1989; 93(12):4878-81.
57. Mohilner DM, Argersinger WJ, Adams RN.. *J Am Chem Soc.*1962; 84(19):3618, 1962.
58. Stejskal J, Kratochvíl P, Jenkins AD*Polymer.*. 1996; 37(2):367-9.

59. Tzou K, Gregory RV. *Synth Metals*. 1992; 47(3):267-77.

60. S. Ramirez and A.R. Hillman, J. Electrochem. Soc., 145 (1998) 2640.

61. Gomes MAB, Gonçalves D, De Sousa ECP, Valla B, Aegerter MA, Bulhões LOS.. *Electrochim Acta*. 1992; 37(9):1653-6.

62. Wang YZ, Joo J, Hsu CH, Epstein EJ.. *Synth Metals*. 1995: 68(3):207-11.

63. Anand J, Palaniappan S, Sathyanarayana D N.. *Polymer*. 1998; 39(26):6819-25.

64. .L.J. Buckley, and K.E. Dudeck, Synth. Met. 1992,**52**,353

65. J. Joo, S.M. Long, J.P. Pouget, E.J. Oh, A.G. MacDiarmid, A.J.Epstein, Phys. Rev. B 57 (1998) 9567.

66. H.S.Nalwa Handbook of organic conductive Molecules and Polymer 1997 :Vol 3 chapter 8

67. Nicholas J. Pinto, Ghanshyam P. Sinha , Fouad M. Aliev Synthetic Metals (1998) 94 199-203

Chapter 4

Effect of preparation techniques on the morphology and dielectric properties of Polyanilines

4.1 INTRODUCTION

Study of polymer systems having special properties is a field of increasing scientific and technical interest, offering the opportunity to synthesize a broad variety of promising new materials with a wide range of electrical and magnetic properties. Technological uses depend crucially, on the reproducible control of the molecular and supramolecular architecture, of the macromolecule via a simple methodology of organic synthesis. Polyaniline (PAni) is one such polymer, it is a typical phenylene based polymer having a flexible -NH- group in a polymer chain flanked either side by phenylene rings. The protonation and deprotonation and various other physico-chemical properties of the polyaniline are attributable to the presence of the -NH- groups. Polyanilines have been studied extensively in the last few decades with improvements coming in the quarters of processing. It plays the key role in establishing the intrinsic electrical properties, dependent on crystallinity and orientation. Since the discovery of enhanced processibility of PAni many studies have been performed on the system and related analogues. The fibre form of these conducting systems in spite of its better properties is rarely studied owing to the difficulty in fabrication. But a concomitant attempt to generate a similar structure through a morphological change had been well received

PART I

4.2 EFFECT OF SULPHONIC ACIDS AND CHIRAL SUGARS: MORPHOLOGICAL CHANGES

4.2.1 INTRODUCTION

Since the discovery of the first molecular wire of carbon nanotubes[1], molecular wires have attracted much attention because of their novel properties and applications in molecular and electro-optical devices[2]. In fact, conducting polymers themselves can be considered molecular wire. Unfortunately, only the granular morphology of conducting polymers synthesized by a conventional method has been observed. Thus, the synthesis of microtubules or molecular wires of conducting polymers is undoubtedly attractive and significant. A method termed *template synthesis* has been used to obtain microtubules of conducting polymers. This method is an effective way of synthesizing microtubules of conducting polymers, and it has been applied to the synthesis of microtubules of polyacetylene[3], polypyrrole[3,4] poly(3-methylthiophene)[5], polyaniline (PAni)[6,7], and even metallic materials[8,9]. Obviously, the template synthesis method has the advantage of providing a nanotube of regular length and diameter, which can be controlled by a template. However, the template method is not as convenient because a suitable microporous membrane to serve as the template for microtubular formation and a molecular anchor to be used for binding a nascent polymer to the wall have to found, and the template membranes must be removed after polymerization. Recently, Huang and Wan[10] found that conducting microtubules of PAni can be synthesized by *in situ* doping polymerization (ISDP) in the presence of β-naphthalenesulfonic acid (NSA) as the dopant. Compared to the template synthesis method, the ISDP method is a simple way to synthesize microtubules of conducting polymers because the microporous membrane and molecular anchor can be left out. However, conducting polymers having tubular morphology was exclusively formed under these conditions.

Chiral nanotubes of polyaniline (PAni) were successfully synthesized by a template-free method in the presence of (*S*)-(2)-2-pyrrolidone-5-carboxylic acid [(*S*)-PCA)] or (*R*)-(1)-2-pyrrolidone-5-carboxylic acid [(*R*)-PCA] as the dopant for the first time. The tubular morphologies of the resulting PAni–(*S*)-PCA and

PAni-(*R*)-PCA were confirmed by SEM and TEM images. The tubes are 80-220 nm in outer diameter and 50-130 nm in inner diameter. It was proposed that the micelles of aniline-(*S*)-PCA or (*R*)-PCA, which were formed due to the hydrophobic aniline and the hydrophilic -COOH group of PCA, played a "template" role during the formation of the chiral nanotubes. These chiral nanotubes showed optically active and electrical properties. In particular, a positive and a negative Cotton effect corresponding to a helical screw of the polymer main chains was observed in the chiral nanotubes. The structural characterization measured by FTIR and X-ray diffraction indicated that the configuration of PCA did not affect the main chains of the chiral nanotubes; however, short-range ordering at 2h = 6.43 (d = 13.73 A°) was significantly observed from the chiral nanotubes, which might result from the chiral character of the dopant[11]. The phenomena of optical rotation and circular dichroism were discovered during the 19th century and led to the concept of chirality. This is an electromagnetic phenomenon rather than an especially optical one[12]. More recently, chiral materials have received considerable attention. The main reason is the success in making composite materials that are chiral in the microwave frequency band. With their unique electromagnetic properties, chiral composite materials might have potential applications in the fields of microwave absorption materials, antennae and microwave devices[13]. A study on measuring the electromagnetic parameters of chiral materials has been carried out by Sun et al[14].

Recently, chiral conducting polymers have attracted considerable interest because of their potential applications such as electrodes for electrochemical asymmetric synthesis[15,16] modified electrodes capable of performing stereoselective analysis[17,18], novel chiral stationary phases for chromatographic separation of enantiomers[19-21], microwave absorbents[22] and electroactive chiral membranes for selective transport of enantiomers[23]. Optically active conducting polymers of PPy[24-27], polythiophene (PTH)[28-30] and Pani[31-36]have been reported in the literature. However, the morphologies of these chiral conducting polymers have seldom been investigated, and only granular morphologies (200–600 nm) of chiral conducting PAni were reported[37]. Due to its excellent electronic and environmental stability, facile redox and pH switching between different colored states, PAni is recognized as one of the most promising organic conducting polymers. As to PAni nanotubes, it is important to functionalize them for realizing their wide range of potential applications.

In the present study, we have attempted to study the influence of the dopant to codopant combination on the morphology and dielectric response of polyaniline in the ISM frequency range of 2GHz- 4GHz and high frequency field of .05-13 MHz

4.2.2 EXPERIMENTAL

Freshly distilled aniline was used for the polymerization reactions. Ammonium persulphate (APS) as oxidant and dopants and codopants such as ß-NSA and D-glucose, mannose andsucrose were used as received. The mixed dopant consisted of ß-NSA and D-glucose/other chiral sugars in which 2.62g of ß-NSA and 1.8g of D-glucose were dissolved in 40 and 20 ml deionised water respectively. The synthesis procedure of PAni doped with ß -NSA is as follows: Aniline was added immediately to the dopant mixture solution and an aqueous solution of the oxidant APS is added quickly to the aniline monomer with constant stirring for about 8h. The precipitate formed was then filtered. The residue was washed with water, acetone and methanol several times, and finally oven dried at 50-60°C for about 6h. The tubular morphology of the resulting PAni-NSA was confirmed by scanning electron microscopy (SEM) measurement and carried out on a JEOL scanning Microscope JSM 840A. Further confirmation of the structure of PAni-NSA was done on the basis of FTIR (Perkin-Elmer System) and X-ray diffraction data.

4.2.3 RESULTS AND DISCUSSIONS

4.2.3.1 Characterisation, Morphological and dielectric study of PAni:NSA: Glucose System

From the initial studies on Polyaniline doped with sulphonic acids, the dopant NSA is observed to impart a tubular morphology to the conducting polymer. A slightly more elaborate dielectric study for the organic sulphonic acid doped samples in conjunction with chiral sugars is summarized in the next section.

I. Characterization

[i] IR spectroscopy:

The structures of polyaniline prepared with dopant- codopant system is analyzed by IR spectroscopy. Figure 4.1a and Figure 4.1b shows the IR spectrum of Polyaniline doped with NSA and NSA-glucose codopant respectively. Between the spectra of dopant and dopant-codopant systems, no pronounced differences are observed indicating that the main components of each specimen have the same chemical structure. The quinoid stretching vibrations occur at 1567 cm^{-1} in PAni-NSA and at 1561 cm^{-1} for PAni-NSA-Glucose system.

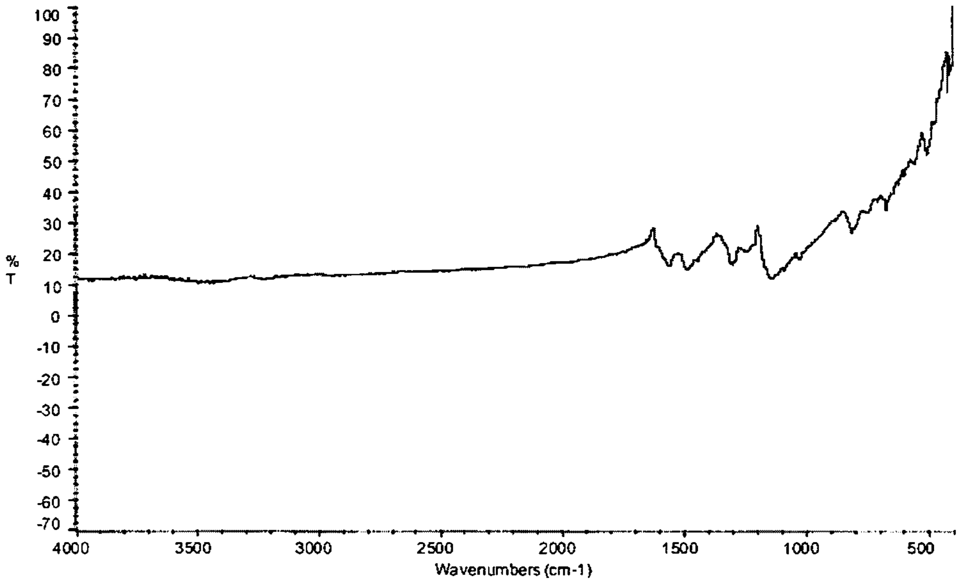


Figure 4.1a: IR spectrum of PAni doped with NSA

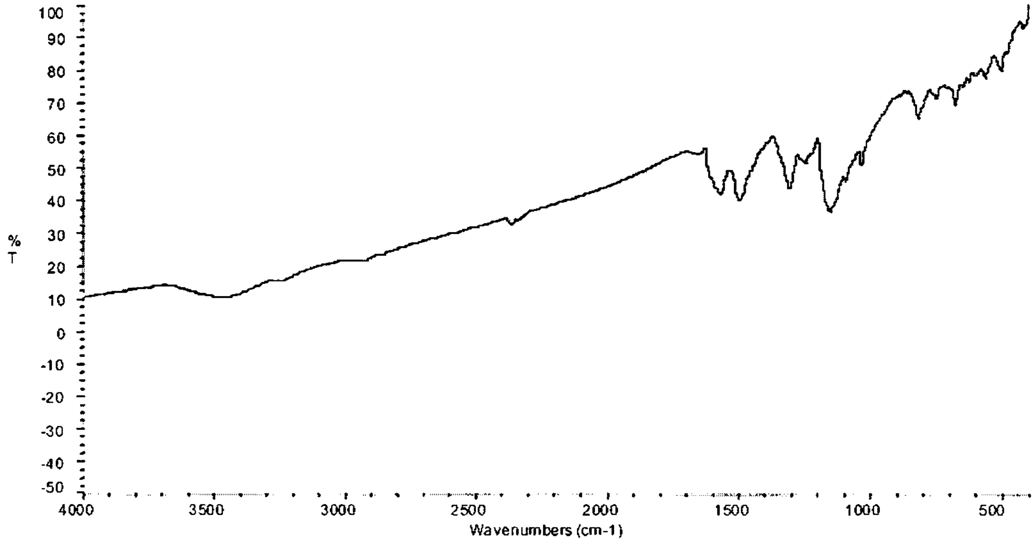


Figure 4.1b: IR spectrum of PAni doped with NSA and Glucose

The benzenoid stretching vibrations occur at a frequency 1494cm^{-1} and 1483 cm^{-1} respectively. The characteristic peak of doped PAni appears at 1152 cm^{-1} in PAni-NSA is shifted to a lower frequency i.e, at 1133 cm^{-1}.

[ii] X-ray Diffraction Analysis [XRD]

Figure 4.2 shows the X-ray Diffraction Analysis of PAni synthesized in NSA-Glucose codopant system. It can be seen from the figure that there is a sharp peak at $2\theta = 25^0$ indicates the presence of more ordered and crystalline structures in Polyaniline prepared using NSA-Glucose codopant system[38].

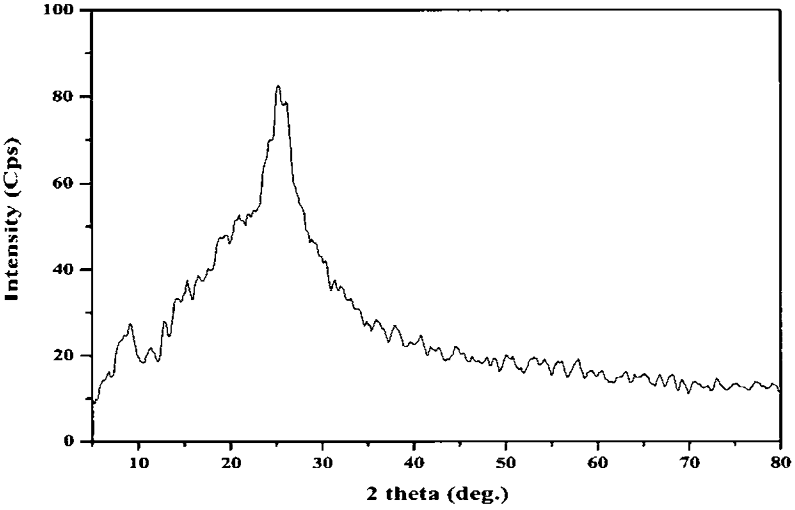


Figure 4.2 : X-ray diffraction pattern of Pani:NSA:Glucose system

[iii] Scanning Electron Microscopy [SEM]

Figure 4.3 shows the SEM micrograph of Polyaniline doped with NSA: Glucose system. It is clear from the micrographs that the polyaniline prepared with NSA dopant imparted a tubular structure to Polyaniline. Figure 4.3 shows that the PAni prepared with NSA:Glucose system yields Polyaniline with uniform tubular morphology. The results indicate that along with a chiral codopant; NSA can give uniform tubular shape to Polyaniline chains, which increases the short-range order and hence increases the crystallinity in Polyaniline. The results are in good agreement with the XRD analysis

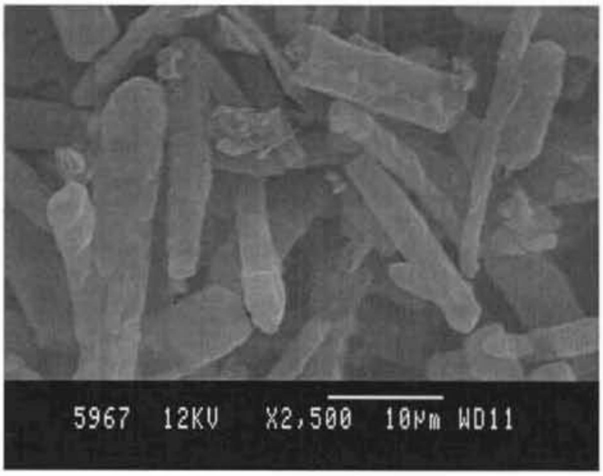


Figure 4.3: Scanning Electron Micrograph of PAni doped with NSA and glucose

.*[iv] Thermal Characterization*

Figure 4.4 shows the TGA thermogram of Pani:NSA:Glucose. The TGA thermograms of Polyaniline-NSA-Glucose system is shown in figure 4.4. In the case of Polyaniline-NSA-Glucose up to 250°C the degradation is only 10 % due to the evolution of dopant. Then a weight loss of 13 % is observed at 350 °C , which may be due to evaporation of excess glucose molecules and the dopant present in polyaniline. The degradation of polyaniline starts at 350 °C and from that temperature a sharp reduction is observed [21%]. This higher stability for the PAni-NSA-Glucose may be due to the higher crystallinity of Polyaniline. Figure 4.5 shows that the glass transition temperature of Polyaniline is 87°C when it is prepared with NSA-Glucose dopant-codopant system. The crystallization temperature of PAni-NSA-Glucose starts at 104 °C

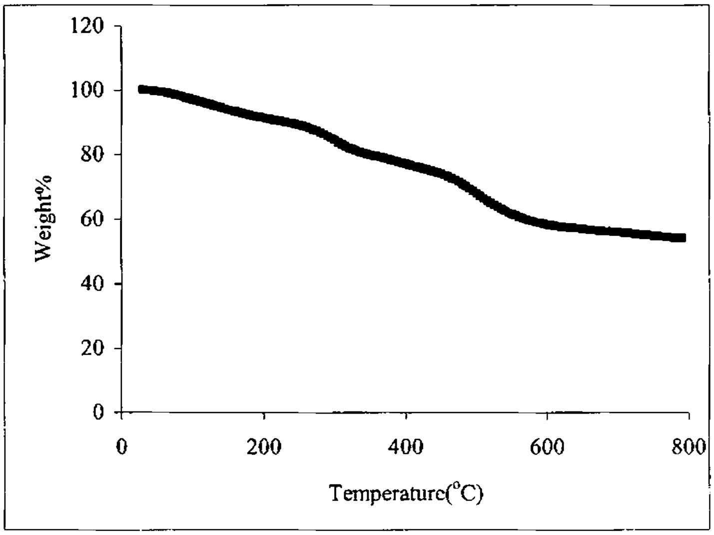


Figure 4.4: TGA thermogram of PAni:NSA:Glucose

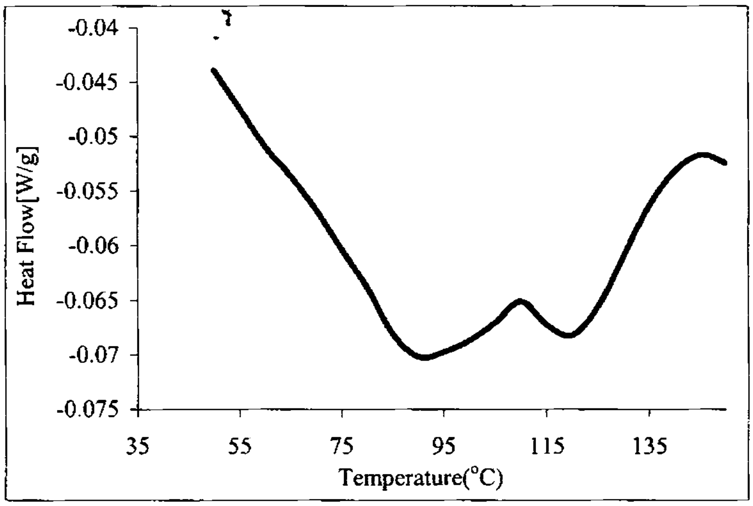


Figure 4.5 DSC thermogram of PAni:NSA:Glucose

4.2.3.2 *Studies with Mannose and Sucrose as codopants*

I Characterisation

[i] Scanning electron microscopy[SEM]

Since the chiral dopant can give the tubular morphology, the synthesis of Polyaniline is carried out in the presence of other chiral sugars like mannose and sucrose. Mannose and sucrose gave tubular morphology as supported by the tubular forms present in SEM micrographs fig 4.6 and 4.7.

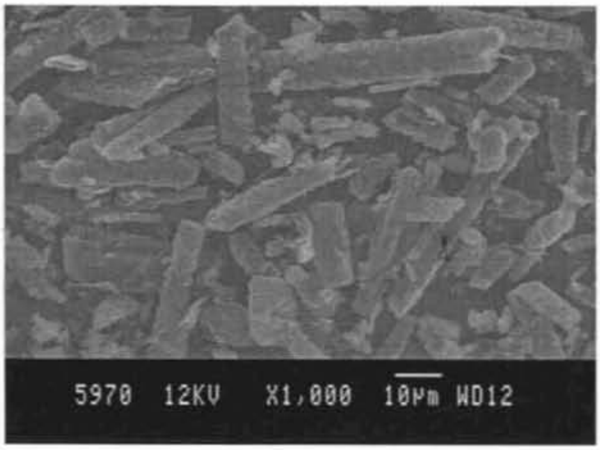


Figure 4.6: Scanning Electron Micrograph of PAni doped with NSA:Mannose

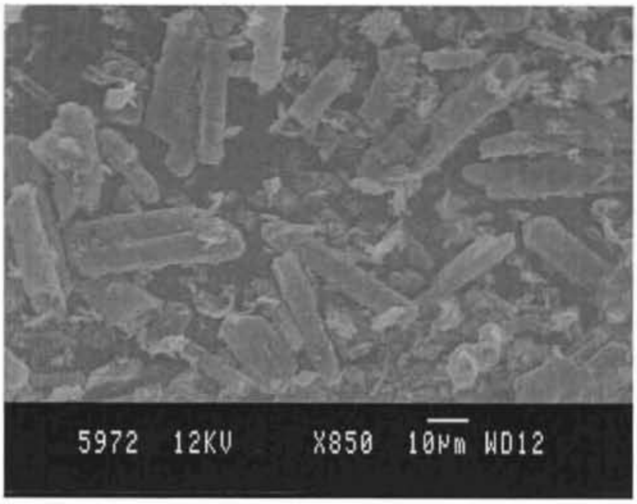


Figure 4.7: Scanning Electron Micrograph of PAni doped with NSA:Sucrose

It is clear from the figures that two systems show tubular morphology but the uniformity in tubular shape is varied. In the case of mannose doped polyaniline [Figure 4.6] is more uniform than those doped with sucrose [Figure 4.7] though less uniform than PAni: NSA:Glucose system.

[ii] Thermal Studies

The TGA thermograms of Polyaniline-NSA-Mannose and Polyaniline-NSA-Sucrose system are shown as Figures 4.8 a and 4.8b respectively. The figure 4.8a indicates that there is a weight loss of 6% for polyaniline-NSA-Mannose due to the evolution of the dopant at 175°C. Then about 3% of weight loss at 275°C which may be due to evaporation of excess glucose molecules and the dopant present in polyaniline. The degradation of polyaniline starts at 275 °C and from that temperature a sharp reduction is observed [32%]. Sucrose codopant system also shows the same trend as shown by the Mannose codopant system as shown in the figure 4.8 b. In Sucrose codopant system, the initial weight loss of 6% is observed up to 200°C.

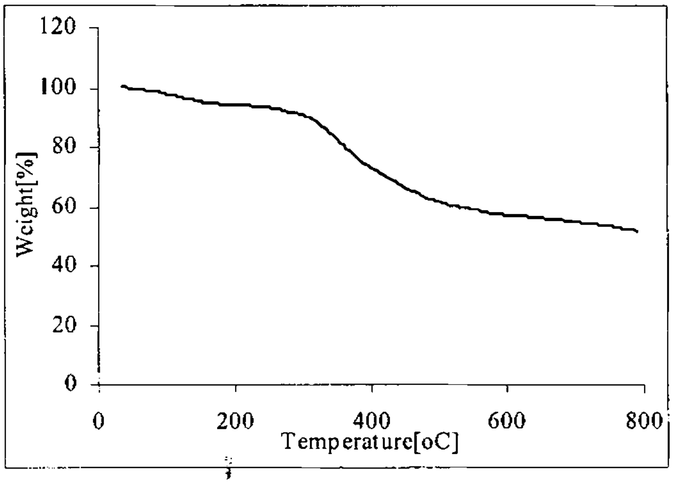


Figure 4.8 a : TGA thermogram of Pani:NSA:Mannose

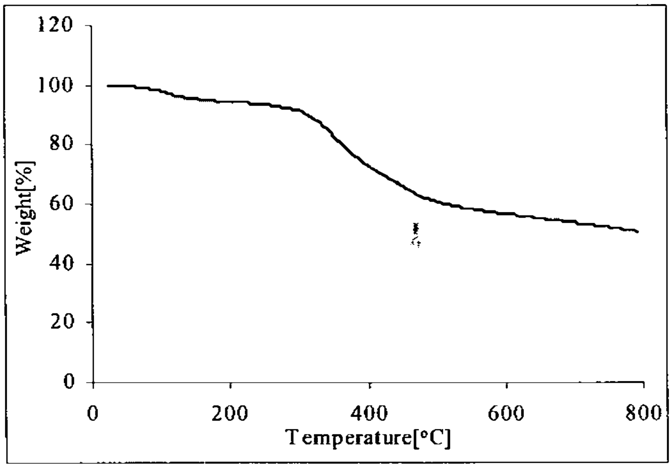


Figure 4.8 b: TGA thermogram of Pani:NSA:Sucrose

Figures 4..9 a and 4.9 b shows Polyaniline prepared using NSA -Mannose and NSA-Sucrose respectively. It is clear from the graphs that the glass transition temperature (Tg-110 °C) of the PAni- NSA -Mannose is shifted to 95°C in Polyaniline prepared with NSA-Sucrose dopant-codopant system. The lower Tg shift of Pani in the NSA -Sucrose system shows that the polyaniline chains are more flexible than Pani-NSA-Mannose. The crystallization temperature of Pani-NSA-Mannose is at 142°C and is shifted to a low temperature in the case of Pani-NSA-Sucrose [104 °C].

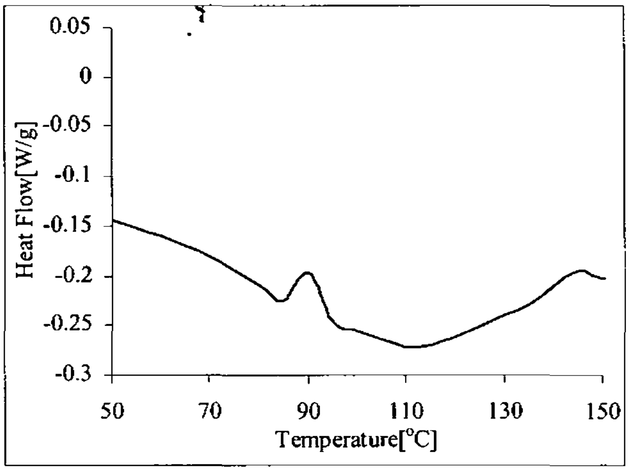


Figure 4.9a: DSC thermogram of PAni:NSA:Mann

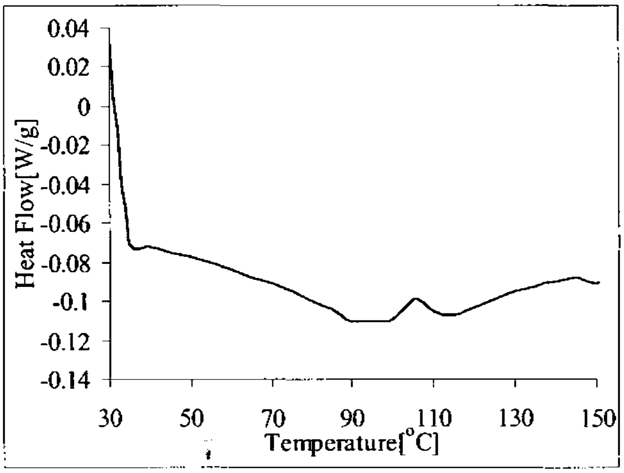


Figure 4.9b: DSC thermogram of PAni:NSA:Sucr

II Dielectric Properties

1. Dielectric loss (ε″) and Conductivity (σ)

Figures 4.10 and 4.11 shows the dielectric loss and conductivity of Polyanilines prepared with PAni:NSA:Glucose, Pan:NSA:Mannose, Pan:NSA:Sucrose respectively.

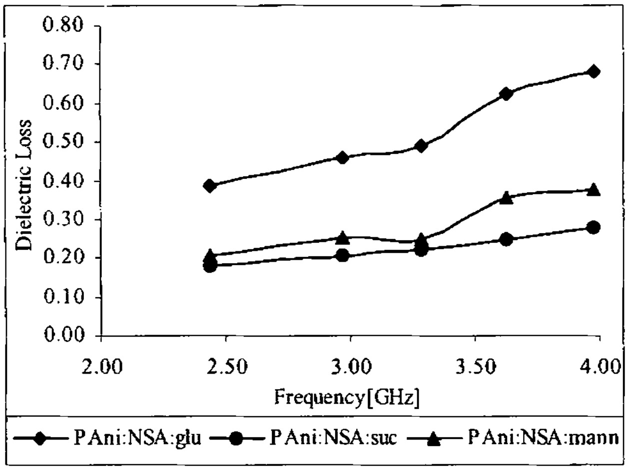


Figure 4.10:Variation of dielectric loss of PAni with frequency

It is clear from the figures that the dielectric loss and conductivity are highefor Polyaniline prepared with PAni:NSA:Glucose . When the size of dopant molecule increases, it will make a conductive path and the intrachain conduction will contribute to the conductivity. In the case of polyaniline prepared with glucose codopant, which gave the uniform tubular morphology, the localization length is high which increases the intrachain conduction. It has been theoretically proved that the intrachain conduction is greater than inter chain conduction· Also the longest polymer gives a higher intrachain carrier displacement probability. It will therefore present higher levels of conductivities[39]. Polyaniline prepared with glucose codopant posses uniform, long, tubular morphology contributes more with intra chain conduction and therefore the dielectric loss and conductivity are high.

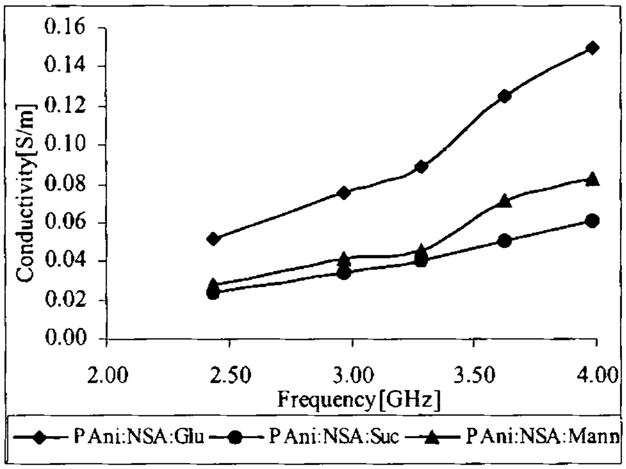


Figure 4.11:Variation of Conductivity of PAni with frequency

It is also clear that the mannose codopant stands at the second position, which gave more uniform structures than sucrose, it confirms the contribution to dielectric loss and conductivity is higher through intra chain conduction than inter chain conduction. It is also clear from the figures that the dielectric loss and conductivity are increased with increase in frequency as in the case of Polyaniline doped with $HClO_4$ dopant.

2. Dielectric constant (ε′)

Figure 4.12 shows that the dielectric constant is also higher for Polyaniline prepared with Glucose codopant. When the size of the dopant molecule increases, the capacitive coupling between the chains decreases and there by the dielectric constant will decreases. Among the three codopants, glucose is smaller in size compared to mannose, which in turn smaller than sucrose. Hence the dielectric constant also follows the same order. It is clear from the figure that the dielectric constant is not much changed with frequency since the sizes of the dopants are comparable.

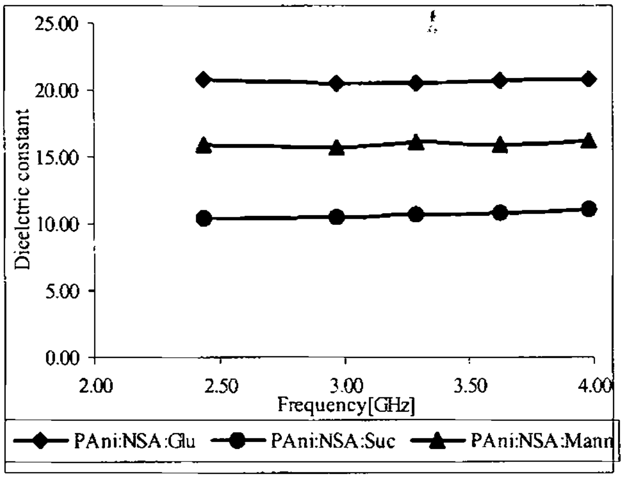


Figure 4.12: Variation of dielectric constant of PAni with frequency

3. Loss tangent (tan δ) and Dielectric heating coefficient (J)

The loss tangent is directly related to the dielectric loss and the dielectric heating coefficient is inversely related to the dielectric loss. Polyaniline with Glucose codopant gives higher value for loss tangent and the minimum value for dielectric heating coefficient as shown in the figure 4.13 and 4.14 respectively. Figure also shows that the loss tangent is increased with frequency and the dielectric heating coefficient is decreased with frequency.

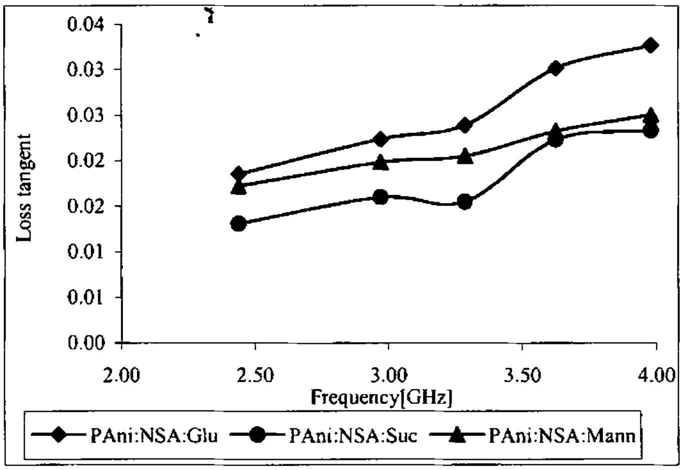


Figure 4.13:Variation of Loss Tangent of PAni with frequency

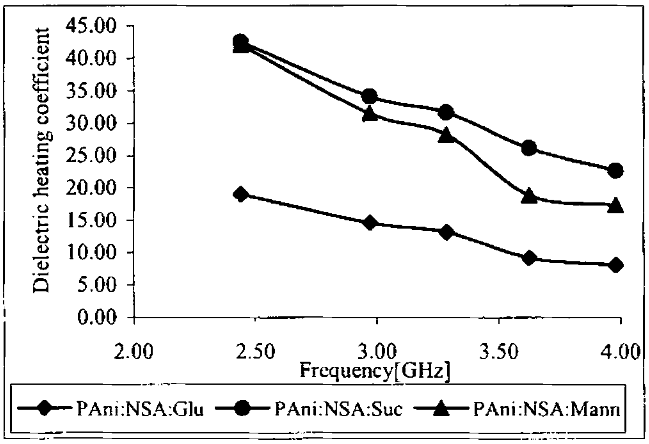


Figure 4.14:Variation of dielectric heating coefficient of PAni with frequency

4. Absorption coefficient and Penetration Depth

Figure 4.15 and 4. 16 show that the absorption coefficient and Penetration depth of Polyaniline prepared with three codopants. It is clear that the absorption coefficient is higher for PAni:NSA:Glucose and the penetration depth or skin depth is minimum for the same. The explanation is same as that given in chapter 3. Since the absorption coefficient is directly related to the dielectric loss and loss tangent, it is increasing with frequency and the skin depth follows the reverse order.

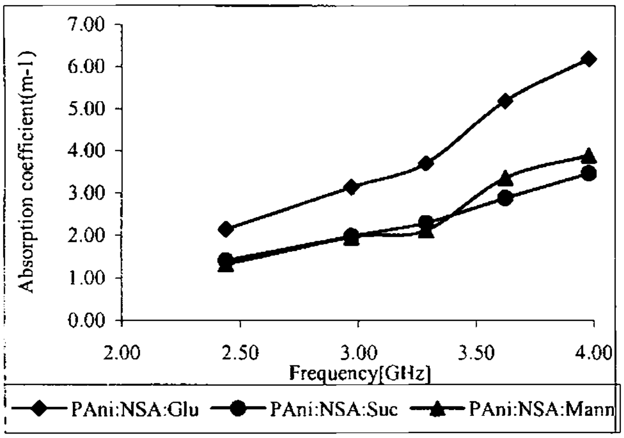


Figure 4.15:Variation of Absorption coefficient of PAni with frequency

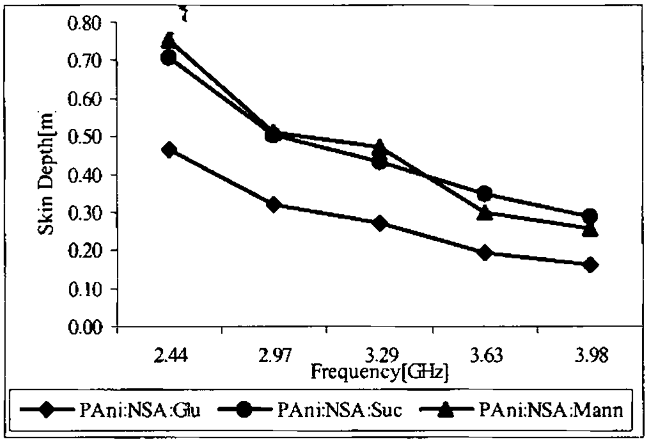


Figure 4.16:Variation of Skin depth of PAni with frequency

Based on the previous studies [chapter 3], CSA doped Polyaniline shows better dielectric properties in the microwave field compared to other organic dopants, Polyaniline with CSA dopant and Glucose codopant is prepared, which is found to give the uniform morphology.

4.2.3.3 Characterization and dielectric properties of Pani:CSA:Glucose system

I. Characterization of PAni:CSA:Glucose system

[i] Scanning Electron Microscopy [SEM]

Figure 4.17 shows the SEM micrographs of Polyaniline prepared CSA:Glucose codopant system. It is clear from the figures that no tubular morphology is obtained for Polyaniline but it imparted more uniformity to Polyaniline.

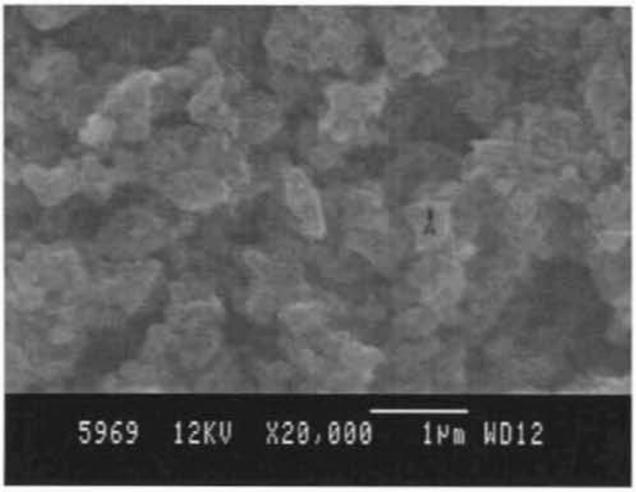


Figure 4.17: Scanning Electron Micrograph of PAni doped with CSA:Glucose

[ii] X-Ray Diffraction Analysis [XRD]

Figure 4.18 shows the XRD analysis of polyaniline prepared with CSA-Glucose codopant system. It is clear from the figure that the broad bands at 14°, 17 °, 22 ° and 25 ° indicating that the polymer formed posses less crystalline phases.

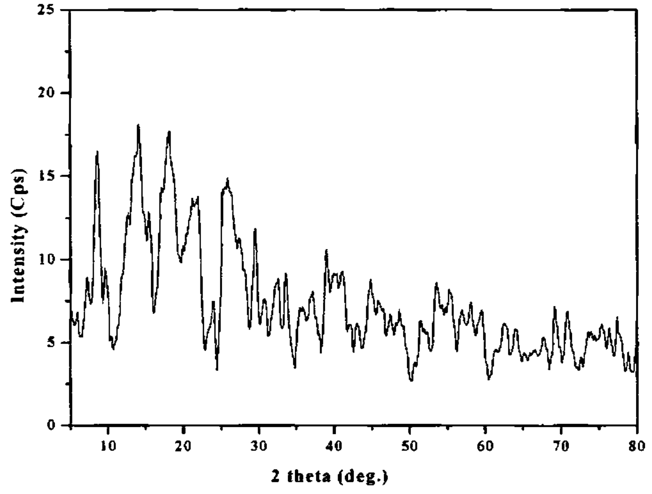


Figure 4.18: XRD graph of PAni doped with CSA:Glucose

[iii] Thermal Characterization:

Figure 4.19 and 4.20 shows the TGA thermogram and DSC thermogram of Polyaniline-CSA-Glucose system. The figure 4.19 indicates that there is a weight loss of 9% due to the evolution of the dopant at 225°C. Then about 11% of weight loss at 350°C which may be due to evaporation of excess glucose molecules and the dopant present in polyaniline. The degradation of polyaniline starts at 350 °C and from that temperature a degradation of 22% is observed up to 650°C. The thermal stability of CSA doped samples are much higher compared to NSA doped samples.

Figure 4.20 shows that the glass transition temperature of Polyaniline prepared using CSA: Glucose is 114 °C and the crystallization temperature is 119 °C .

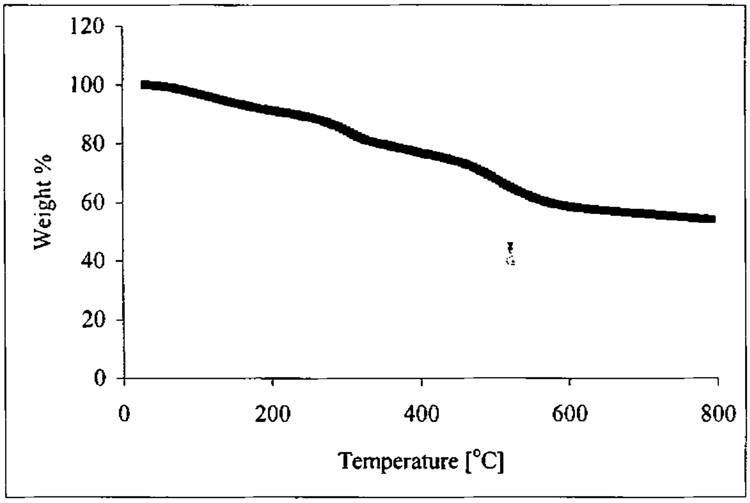


Figure 4.19:TGA thermogram of PAni:CSA:Glucose

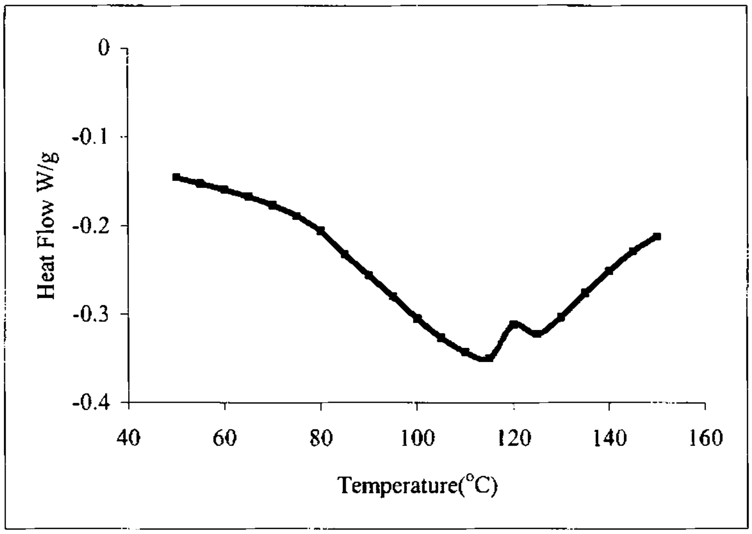


Figure 4.20: DSC thermogram of PAni:CSA:Glu

II Dielectric properties of PAni:CSA:Glucose system

Table 4.1 shows the variation of dielectric properties of PAni:CSA:Glucose system with frequency. The dielectric loss, conductivity, loss tangent and absorption coefficient are increasing with frequency and the dielectric constant, dielectric heating coefficient and the skin depth are decreasing with frequency.

Table 4.1:Variation of dielectric properties of PAni:CSA:Glucose with frequency

Dielectric property	**Frequency [GHz]**				
	2.44	2.97	3.29	3.63	3.98
Dielectric Loss (ε''_r)	3.20	3.61	3.78	4.10	3.97
Conductivity(σ S/m)	.43	.59	.69	.82	.88
Dielectric Constant(ε'_r)	16.65	14.81	15.23	15.22	15.15
Dielectric Heating Coefficient (J)	.71	.56	.53	.47	.49
Loss Tangent (tan δ)	.19	.24	.25	.27	.26
Absorption Coefficient (m^{-1})	19.76	28.68	32.76	39.06	41.64
Skin Depth (m)	.05	.03	.03	.03	.02

All phenomenon are similar to that observed for conducting Polyaniline and the explanations are applicable to this matrix too.

4.2.3.4 Comparison between various dopant: codopant combinations for Polyaniline

Table 4.2: Variation in dielectric property of PAni: NSA: Glucose and PAni: CSA: Glucose

Dielectric property	**PAni :NSA:Glu**	**PAni :CSA:Glu**
Dielectric Loss (ε''_r)	**.46**	3.61
Conductivity(σ S/m)	**.08**	.59
Dielectric Constant(ε'_r)	**20.45**	14.81
Dielectric Heating Coefficient (J)	**14.62**	0.56
Loss Tangent (tan δ)	**.02**	.24
Absorption Coefficient (m^{-1})	**3.13**	28.68
Skin Depth (m)	**.32**	.03

Table 4.2 shows the dielectric properties of Polyaniline prepared with NSA:Glucose system and CSA:Glucose system, which gives the best results. Between the two systems, Polyaniline prepared with CSA:Glucose posses high dielectric loss and conductivity. When a microwave is passed through the material, the dipoles align along the direction of applied field resulting in orientation polarization. The chains are thickly packed or more crystalline; this orientation of dipoles with the external field becomes less. It is clear from the SEM micrographs and XRD analysis [that the CSA doped Polyaniline has shorter grain size and lesser crystallinity than NSA doped samples. Since the dielectric properties of conducting polymers in the microwave field are depended on these orientation polarizations, the dielectric properties of CSA:Glucose doped Polyaniline shows better results.

PART II

4.3 STUDIES ON POLY [o-TOLUIDINE] : EFFECT OF DOPANTS AND CODOPANTS

I. Characterization

[i] Scanning Electron Microscopy [SEM]

Figures 4.21 a, b, c, d shows the scanning electron micrograph of PoT-NSA, PoT-NSA-Glucose, PoT-NSA-Mannose and PoT-NSA-Sucrose respectively. It is clear from the micrographs that PoT -NSA samples does not show a tubular morphology, as in the case of Pani-NSA system. The presence of -CH3 group in each benzene ring push apart the dopant and it make more disorderd system as shown in the figure. The chains are arranged in layers and are loosely packed in PoT-NSA system. In the case of PoT-NSA-Codopant system, the poly o-toluidine chains are more thickly packed up, and the with Glucose codopant, a very few number of chains are in short tubular shape. In the case of mannose and sucrose, no such indication of tubular shapes as shown in the figures.

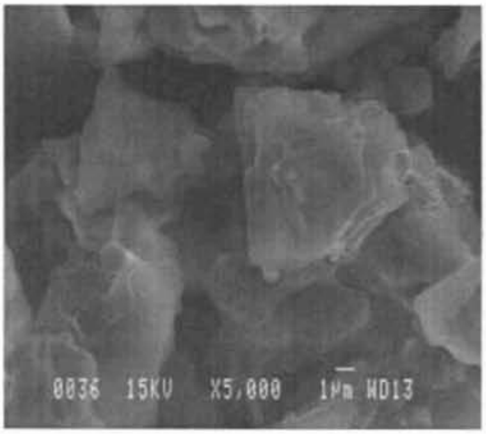


Figure 4.21a PoT:NSA

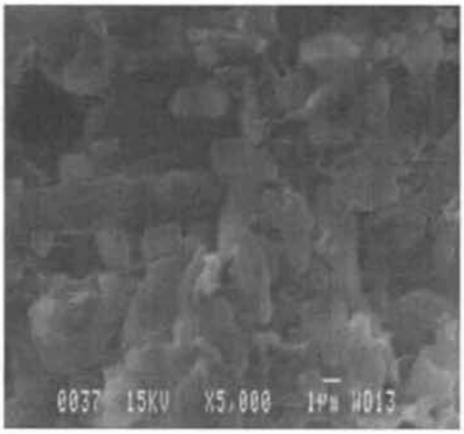


Figure 4.21b PoT:NSA:Glucose

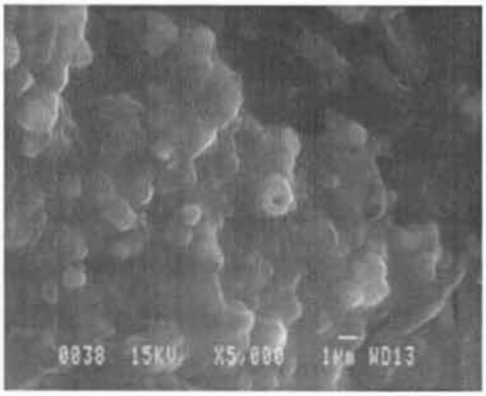


Figure 4.21c PoT:NSA:Mannose

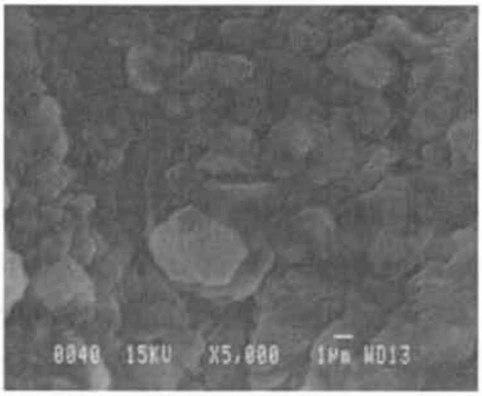


Figure 4.21d PoT:NSA:Sucrose

1. Dielectric Properties

Figure 4.22 shows the dielectric loss and conductivity of Poly o--toluidine prepared with NSA, PoT:NSA:Glucose, PoT:NSA:Mannose, PoT:NSA:Sucrose respectively. It is clear from the figure that the dielectric loss and conductivity are higher for Poly-toluidine prepared with PoT:NSA:Glucose . The explanation for this behaviour is same as that given for Pani-NSA-Glucose.

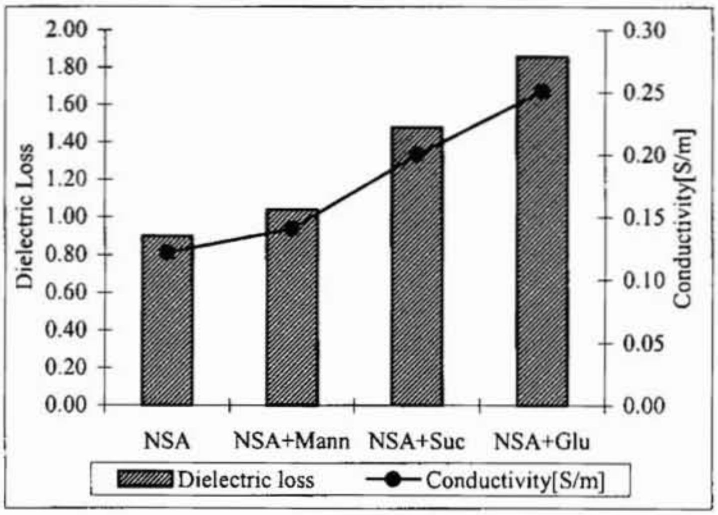


Figure 4.22: Effect of dopants on the dielectric loss and conductivity of PoT at 2.97GHz

Figure 4.23 shows that the dielectric constant is also higher for Poly o-toluidine prepared with NSA and NSA-Glucose codopant. When the size of the dopant molecule increases, the capacitive coupling between the chains decreases and there by the dielectric constant will decreases, and therefore without a codopant shows high value for dielectric constant. It is clear from the figure

4.24 that the loss tangent is high and dielectric heating coefficient is low for PoT-NSA-Glucose system, as expected. Figure 4.25 shows the variation of absorption coefficient and skin depth of PoT prepared in NSA: codopant systems. It also shows the same behavior as that of polyaniline.

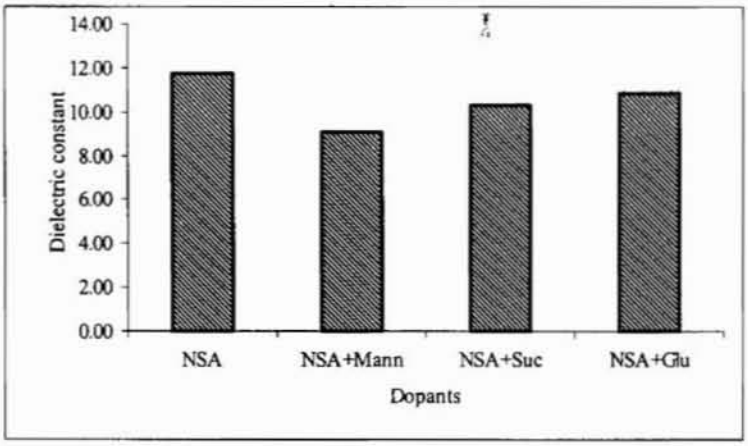


Figure 4.23: Effect of dopants on the dielectric constant of PoT at 2.97GHz

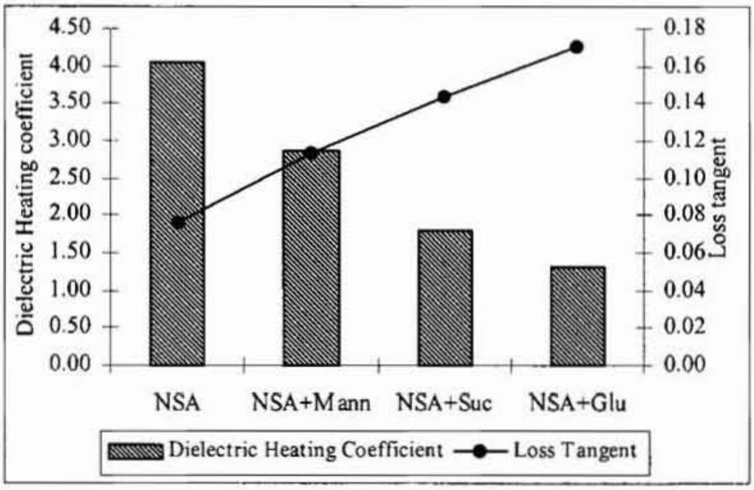


Figure 4.24: Effect of dopants on the dielectric heating coefficient and Loss tangent of PoT at 2.97GHz

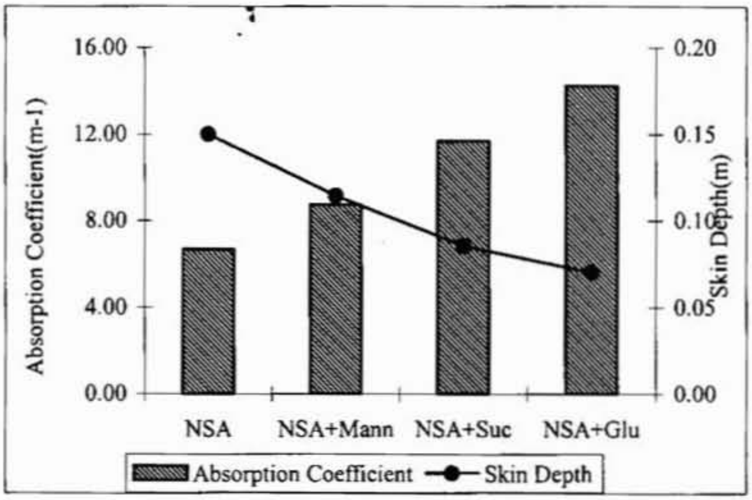


Figure 4.25: Effect of dopants on the Absorption coefficient and Skin depth of PoT at 2.97GHz

PART II

4.4 PREPARATION OF POLYANILINE VIA THE EMULSION POLYMERIZATION PATHWAY

4.4.1 INTRODUCTION

The technique of (macro) emulsion and microemulsion polymerization which are usually used for the preparation of polymer particle are based on a kinetic control during the preparation, the particles are built from the center to the surface, and the particle structure is governed by kinetic factors. Because of the dictate of kinetics, serious disadvantages such as lack of homogeneity and restrictions in the accessible composition have to be accepted. With the concept of "nanoreactors" where the essential ingredients for the formation of the nanoparticles on can take advantage of a potential thermodynamic control for the design of nanoparticles. This means that the droplets have to become the primary locus of the nucleation of the polymer reaction. The polymerization in such nanoreactors should take place in a highly parallel fashion, i.e. the synthesis is performed in 10^{18} - 10^{20} nanocompartments which are separated from each other by a continuous phase. Miniemulsions are dispersions of critically stabilized oil droplets with a size between 50 and 500 nm prepared by shearing a system containing oil, water, a surfactant and a hydrophobe. Polymerizations in such miniemulsions, when carefully prepared result in latex particles which have about the same size as the initial droplets, as could be shown by a combination of SANS, surface tension measurements and conductometry. This means that the appropriate formulation of a miniemulsion suppresses coalescence of droplets. The polymerization of miniemulsions extends the possibilities of the widely applied emulsion polymerization and provides advantages with respect to copolymerization reactions of monomers with different polarity, incorporation of hydrophobic materials or with respect to the stability of the formed latexes.

Polyaniline (PAni) latex particles have been synthesized using both inverse and direct miniemulsion polymerization techniques. It is shown that inverse miniemulsions of aniliniumhydrochloride can be oxidized by simple H_2O_2, thus resulting under optimized conditions in highly crystalline PAni particles dispersed in hydrocarbons with high volume fraction. The resulting structure is identified as emeraldine, which however crystallizes in a new crystal morphology. Oxidation of aniline miniemulsions in water with diverse oxidants from the continuous phase also leads to highly crystalline PAni, which however has a low colloidal stability. Additional employment of a costabilizer in this case leads to stable aqueous PAni dispersions with for water-based systems otherwise unreached local structural order[39]

Dispersions of particles of different conjugated semiconducting polymers such as a ladder-type poly(*para*-phenylene) and several soluble derivatives of polyfluorene could be prepared with well controllable particle sizes ranging between 70 - 250 nm. Layers of these particles formed by spincoating exhibit a particulate structure, revealing the shape of the individual polymer nanoparticles. Annealing above the polymer's glass transition temperature results in coalescing of particles and larger domains of continuous structure are formed. Polymer layers can exhibit significantly improved performances if they possess a multicomponent phase-separated morphology[40,41,42].

Two novel approaches were used to control the dimensions of phase separation in polymer blend layers, both relying on polymer nanospheres prepared by the microemulsion process. In the first approach, heterophase solid layers are prepared from an aqueous dispersion containing nanoparticles of two polymers, while in the second approach, both polymers are already contained in each individual nanoparticle.

4.4.2. EXPERIMENTAL

(i) Preparation of oil water microemulsion: Typically as in emulsion polymerization, the microemulsion was prepared using a solution of Napthenic oil containing oleic acid to which, water-containing ammonia in very low concentration was added. On addition of ammonia, ammonium oleate was formed thereby stabilizing the emulsion.

(ii) Polymerization of Aniline: Aniline was added and stirred well to attain a uniform distribution with in the emulsion. The aqueous solution of the oxidant ammonium persulphate [APS] was added drop wise into the emulsion and the emulsion was allowed to proceed for 24h. When acid doping was employed, Vulcastab was used as a stabilizing agent. During the progress of the reaction the colorless emulsion turns green. The dark green Polyaniline solution was then added to an excess of acetone in order to break the solution and precipitate the Polyaniline salt. It was filtered and washed with acetone, and methanol and then oven dried for about 4h at a temperature of around 50-60°C. The structure was confirmed by FTIR analysis. The TGA and DSC thermograms were recorded upto 800°C using a TA Q50 thermal analysis system at a heating rate of 20°C/min under nitrogen atmosphere. SEM studies were carried out to understand the morphology of the samples.

4.4.3 RESULTS AND DISCUSSIONS

4.4.3.1 Variation of dielectric properties with change in the concentration of the emulsion prepared

I. Characterization

[i] IR spectroscopy

Figure 4.26 shows the IR spectra of Polyaniline prepared in microemulsion pathway. Figure shows the presence of stretching vibration modes of the quinoid [N=Q=N] structure at 1576 cm^{-1} and benzenoid [N-B-N] at about 1484 cm^{-1}. A peak at 1148 cm^{-1} indicates the formation of HCl doped Polyaniline.

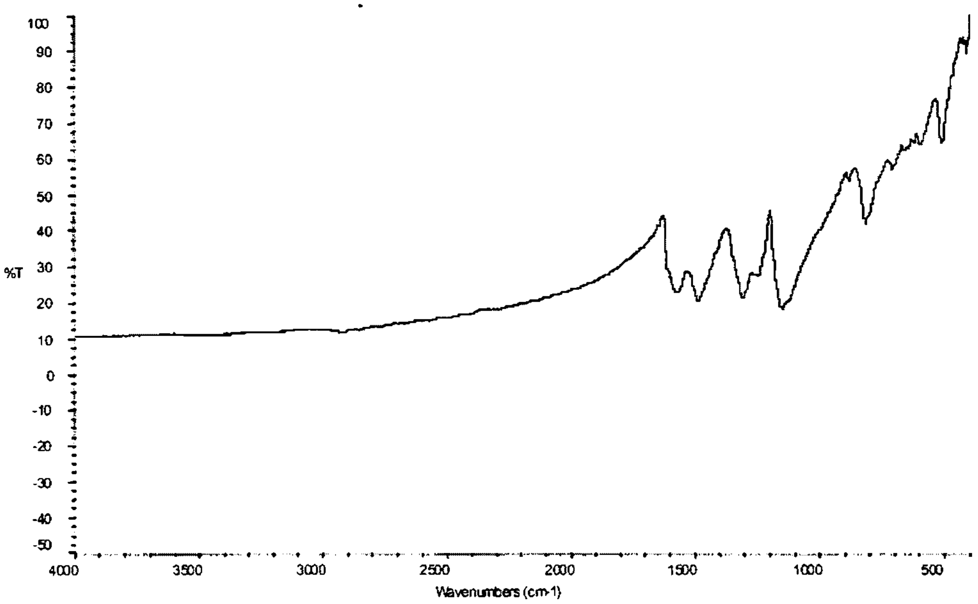


Figure 4.26: IR spectrum of Polyaniline prepared by emulsion pathway

[ii] Scanning Electron Microscopy:

Figure 4.27 .and 4.28 shows the SEM micrographs of Polyaniline prepared in 2.5% and 5% microemulsions. It is clear from the SEM pictures that the Polyaniline prepared in the two different proportions have less size. It is also clear that the Polyaniline prepared in 5 % emulsion is more closely packed and uniform grain size. In the case of 2.5% emulsion, the Polyaniline chains are loosely packed.

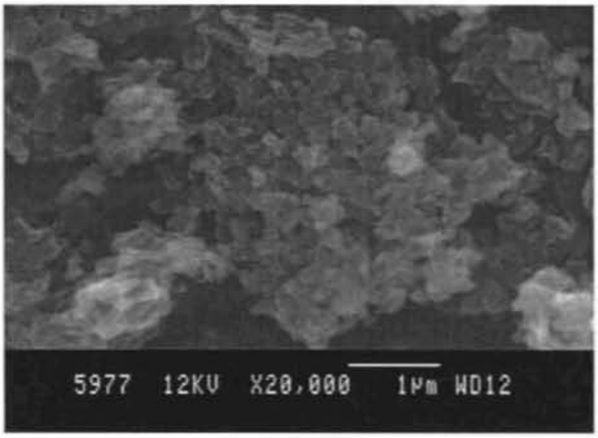


Figure 4.27 Scanning electron micrograph of Polyaniline prepared in 2.5% emulsion

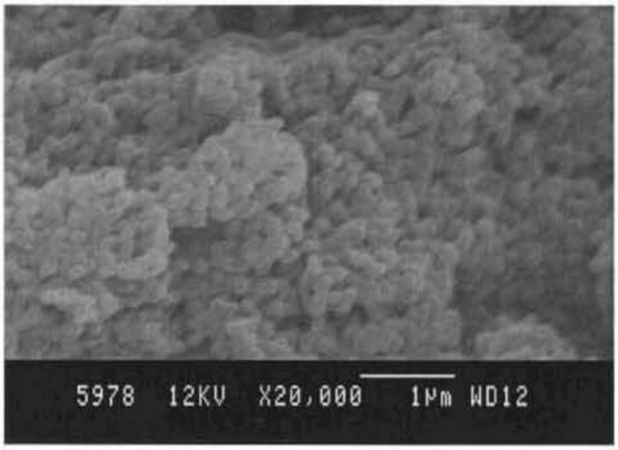


Figure 4.28 Scanning electron micrograph of Polyaniline prepared in 5% emulsion

[iii] X-Ray diffraction Analysis

Figure 4.29 and 4.30 shows the XRD analysis of polyaniline prepared in microemulsions of 2.5% and 5% respectively.It is clear from the figure 4.31 that a sharp peak is observed at 2θ=12° and a broad peak is observed at2θ=25° , indicating the presence of both crystalline and amorphous regions in the polymer. In the case of 5% emulsion, the sharp and intense peaks observed at 2θ=19° and 2θ=25° indicates the presence of more crystallinity in polyaniline prepared with 5% microemulsion.

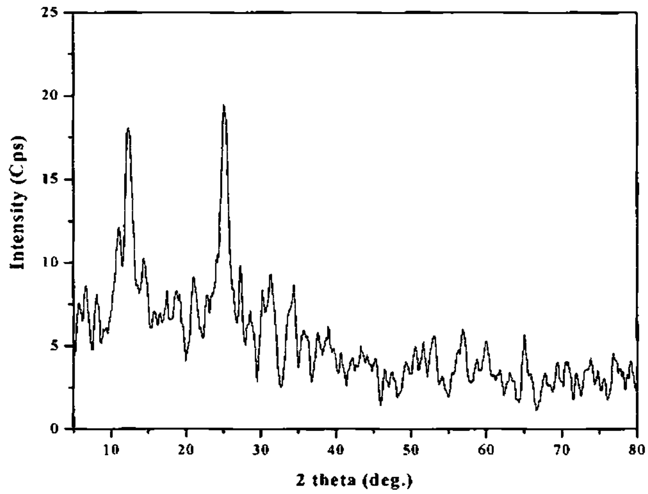


Figure 4.29: XRD graph of 2.5% micro emulsion

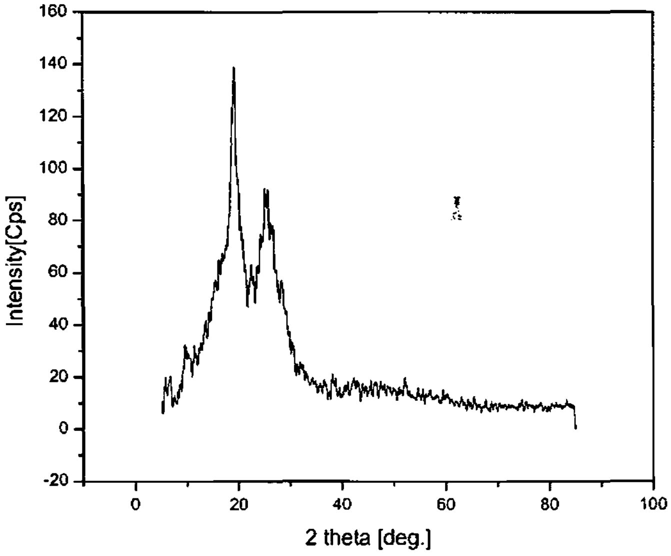


Figure 4.30: XRD graph of 5% micro emulsion

[iv] DSC Analysis

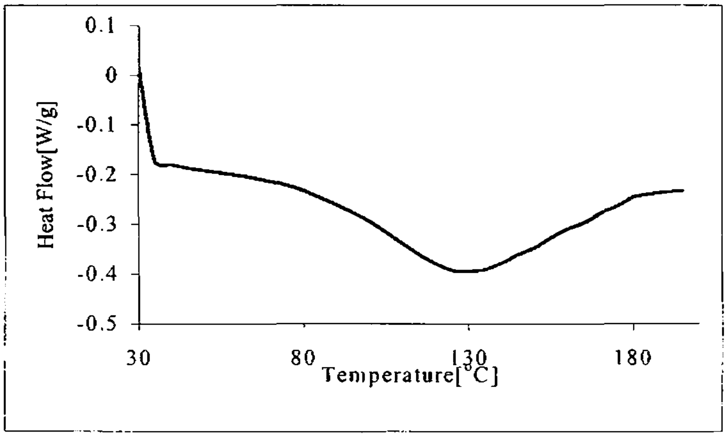


Figure 4.31: DSC thermogram of PAni prepared from 2.5% emulsion

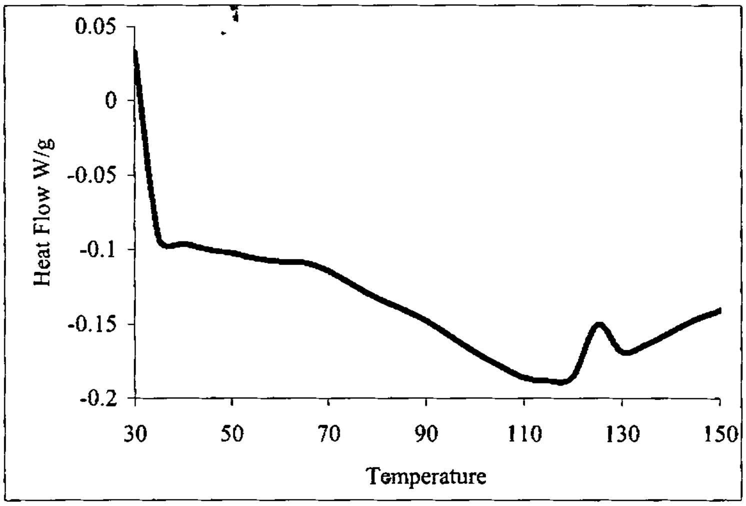


Figure 4.32: DSC thermogram of PAni prepared from 5% emulsion

Figure 4.31 shows that the glass transition temperature (Tg) of 2.5% is 127 °C is shifted to 111°C in 5% sample[figure 4.32]. But there is crystallization of Polyaniline chains is observed in 5% microemulsion at 123 °C, which is absent in 2.5% emulsion indicates the presence of higher percentage of crystallinity in 5% microemulsion.

II. Dielectric properties

1. Dielectric Loss and Conductivity

Figure 4.33 and 4.34 shows the dielectric loss and conductivity of Polyaniline samples prepared in microemulsion. It is clear from the figures that the dielectric loss and conductivity of 2.5% emulsion pathway give higher value than 5%. The dipole alignment is easier when the chains are loosely packed and less crystalline as explained in the case of CSA doped polyaniline samples. The dielectric loss and conductivity is increased with frequency as expected.

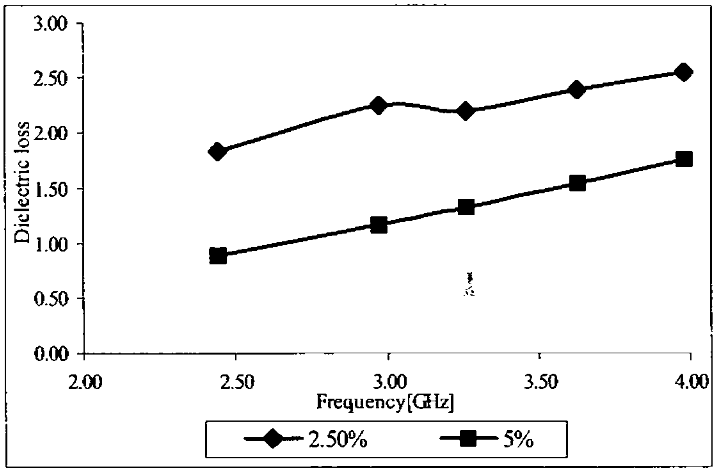


Figure 4.33: Variation of Dielectric loss of PAni with frequency

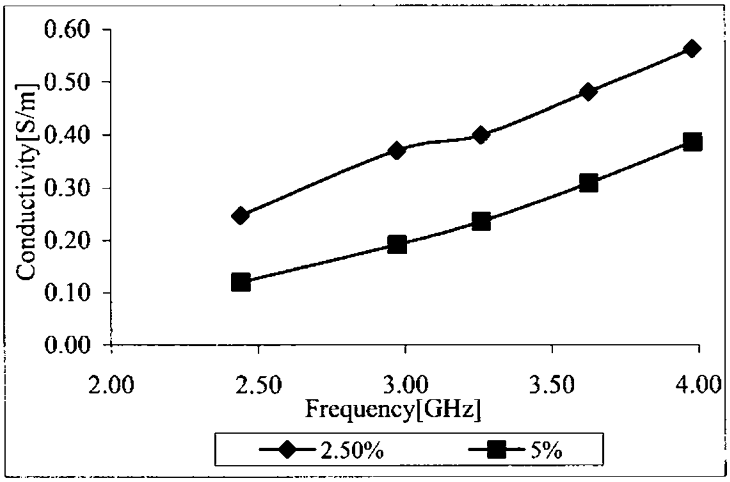


Figure 4.34: Variation of Conductivity of PAni with frequency

2. Dielectric constant:

Figure 4.35 shows that the dielectric constant of 5% emulsion gives the higher value. When the chains are more thickly packed, the inter chain distance reduced and it will leads to a higher capacitive coupling between the chains and thereby the dielectric constant is increased. It is also found that the dielectric constant is decreased with increase in frequency as explained before.

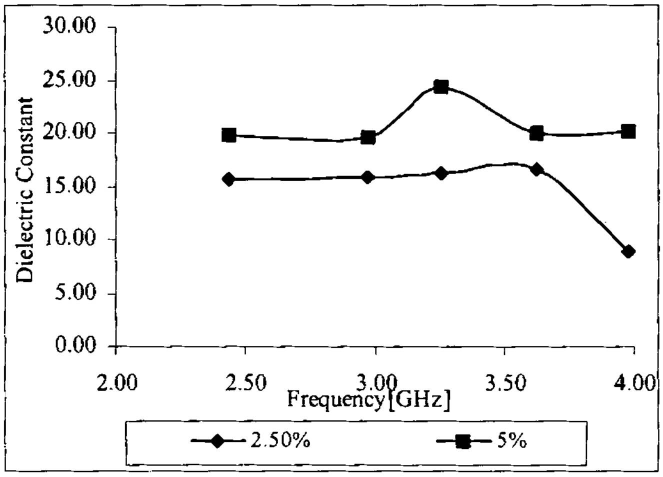


Figure 4.35: Variation of Dielectric constant of PAni with frequency

3. Loss tangent and Dielectric heating coefficient

Figures 4.36 and 4.37 show the loss tangent and dielectric-heating coefficient of Polyaniline prepared in microemulsions respectively. The 2.5 % emulsion shows the higher value for loss tangent and lower value e for heating coefficient. As the heat generation in polymers is due to relaxation loss, the efficiency of heating of a polymer is compared by means of a heating coefficient. The 2.5 % emulsion is the best material for dielectric heating applications.

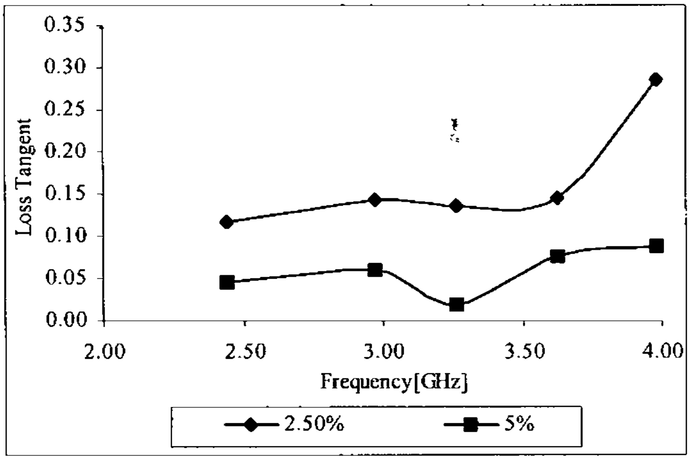


Figure 4.36: Variation of Loss Tangent of PAni with frequency

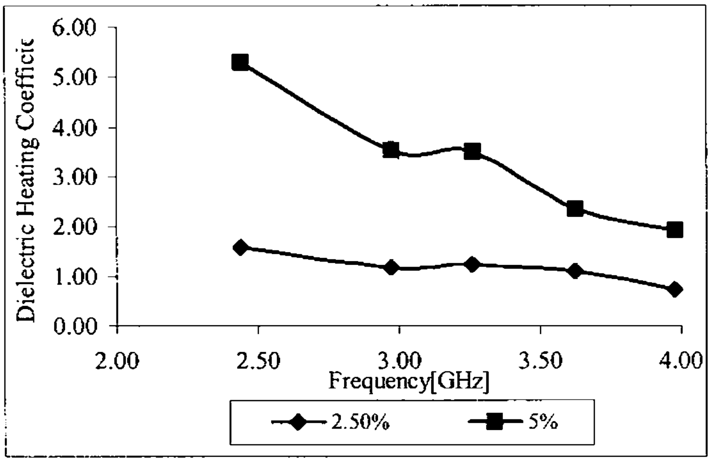


Figure 4.37: Variation of Dielectric heating coefficient of PAni with frequency

4. Absorption coefficient

Figure 4.38 indicates that the absorption coefficient of 2.5% is higher than 5 % emulsion. As the absorption coefficient is derived from the complex permittivity and is a measure of propagation and absorption of electromagnetic waves when it passes through the medium, it is directly related to the dielectric loss.

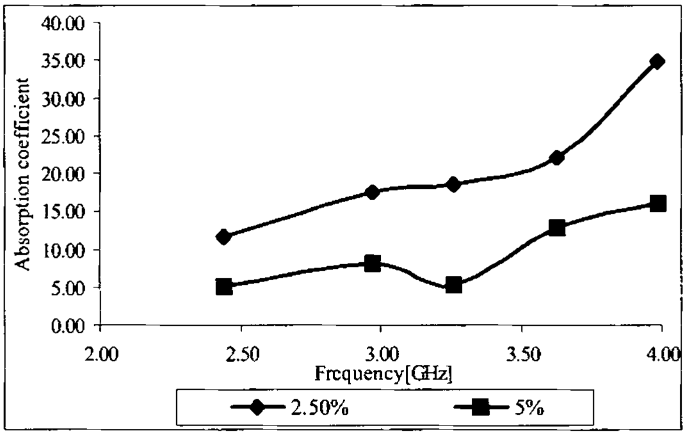


Figure 4.38: Variation of Absorption coefficient of PAni with frequency

4.4.3.2. Comparison of the dielectric properties of doped PAni prepared from 2.5% and 5% emulsion

Dielectric property	**2.5%**	**5%**
Dielectric Loss (ε''_r)	2.25	.037
Conductivity(σ S/m)	.37	.19
Dielectric Constant (ε'_r)	15.80	19.65
Dielectric Heating Coefficient (J)	1.18	3.53
Loss Tangent (tan δ)	.14	.06
Absorption Coefficient (m^{-1})	17.46	8.12
Skin Depth (m)	.06	0.12

PART III

4.5 DIELECTRIC RESPONSE OF POLANILINE PREPARED WITH CHIRAL SUGARS AND MICROEMULSION IN THE HIGH FREQUENCY FIELD

4.5.1 POLYANILINE PREPARED WITH DOPANT-CODOPANT SYSTEM

Figure 4.39 shows the dielectric constant of polyaniline prepared with NSA and chiral sugars [Glucose, Mannose, Sucrose]. It is clear from the figure that the dielectric constant is found to be higher for mannose and sucrose based polyaniline. In the case of glucose based polyaniline, which is more orderly packed and more homogeneous compared to mannose and sucrose based polyaniline. Since the dielectric constant is mainly due to the heterogeneity of materials in the conducting path at high frequency field [MHz field], the dielectric constant is higher for mannose and sucrose based polyaniline. The loss tangent, in the high frequency field, is found to be depend upon the crystallinity of the material and when the crystallinity increases the loss tangent decreases[43] and hence the loss tangent is low for polyaniline prepared with codopants in the MHz range compared to microwave field as shown in the figure 4.40. Figure 4.41 shows that the conductivity increases with increase in frequency, irrespective of the codopant combination and it is found to be high for glucose based polyaniline due to its more ordered structure.

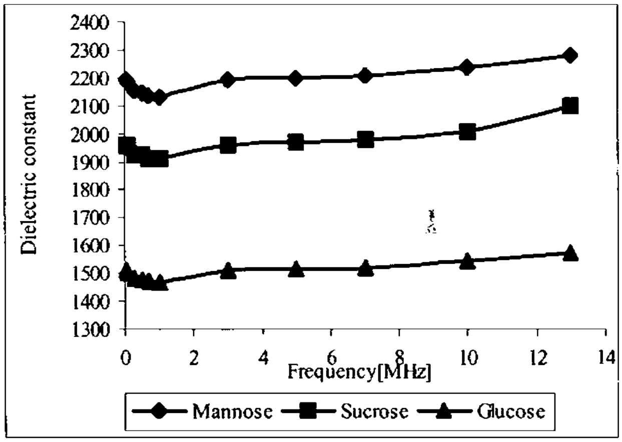


Figure 4.39 : **Variation of dielectric constant of polyaniline prepared using chiral sugars with frequency**

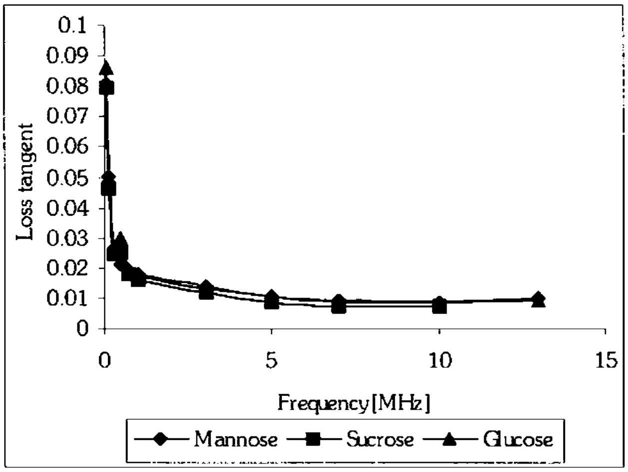


Figure4..40 : **Variation of loss tangent of polyaniline prepared using chiral sugars with frequency**

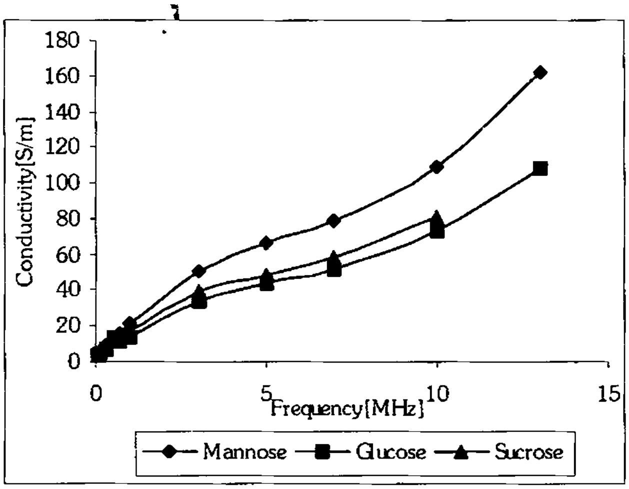


Figure 4.41 : Variation of conductivity of polyaniline prepared using chiral sugars with frequency

4.5.2 POLYANILINE PREPARED WITH 2.5 % MICRO EMULSION SYSTEM

Figure 4.42, 4.43, 4.44 shows the dielectric constant, loss tangent and conductivity of polyaniline prepared with 2.5 % emulsion pathway.

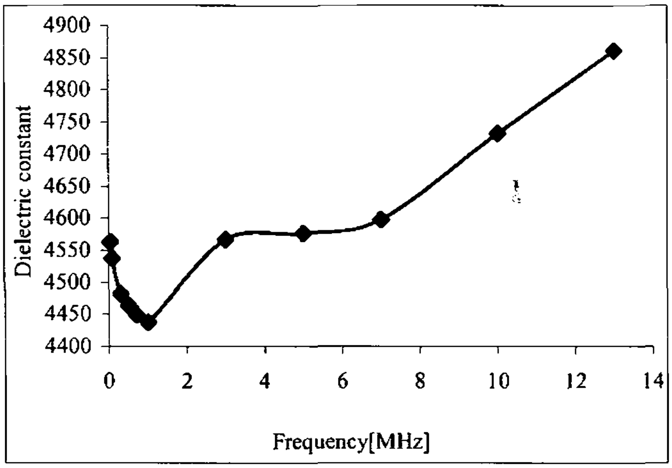


Figure 4..42 : Variation of dielectric constant of polyaniline (2.5% microemulsion)with frequency

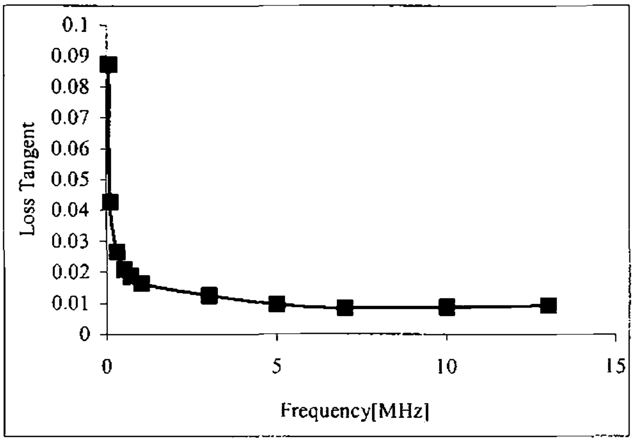


Figure 4.43 : Variation of loss tangent of polyaniline(2.5% microemulsion) with frequency

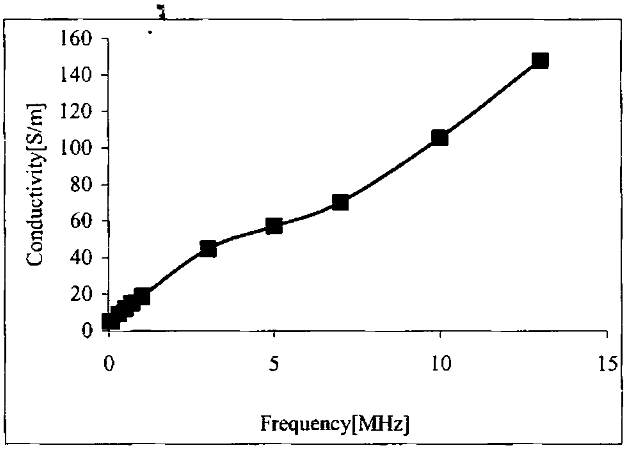


Figure 4..44 : Variation of conductivity of polyaniline (2.5% microemulsion)with frequency

The dielectric constant is found to be higher at the low frequency field [figure 4.42] and is linked to the heterogeneity of materials as explained in the chapter 3. It is also clear from the figure that the dielectric constant is very high for polyaniline prepared with 2.5% emulsion pathway in the high frequency field compared to microwave field. The loss tangent is decreasing with increase in frequency as shown in the figure 4.43. At low frequencies the charge conduction is due to the interaction between the charges among the different chains and the conductivity is found to be increasing with increase in frequency as shown in the figure 4.44.

4.6 CONCLUSIONS

- ⇨ Among the sulphonic acids used as dopants, NSA is found to effect a tubular morphology the polyaniline formed. CSA doped samples was found to respond better in the microwave field than its NSA counterpart.
- ⇨ The effect of various codopants such as chiral sugars glucose, Mannose, Sucrose is employed in the preparation of Polyaniline.
- ⇨ NSA:Glucose and CSA:Glucose gave the best display of properties among the dopant codopant combination.
- ⇨ The methyl derivative of Polyaniline is also prepared in the presence of various chiral sugars and NSA as dopant. PoT:NSA:Glucose shows highest conductivity and dielectric loss.
- ⇨ The chiral sugars showed a positive influence on the dielectric properties of PAni and PoT
- ⇨ PAni is prepared using emulsion polymerization. At varying concentration of the emulsion, PAni is prepared and the dielectric parameters are compared
- ⇨ Better dielectric loss and conductivity is observed for PAni prepared in 2.5% emulsion.

4.7 REFERENCES

1. Lijima, S. Nature 1991, 354, 56.
2. Tabony, J.; Tob, D. Nature 1990, 346, 448.
3. Cai, Z.; Martin, C. R. J Am Chem Soc 1989, 111, 4138.
4. Cai, Z.; Lei, J.; Liang, W.; Menon, V.; Martin, C. R. Chem Mater 1990, 3, 960.
5. Liang, W.; Martin, C. R. J Am Chem Soc 1991, 112, 9666.
6. Parthsarathy, R. V.; Martin, C. R. Chem Mater 1994, 6, 1627.
7. Mennen, V. Synth Met 1993, 55, 1165.
8. Martin, C. R.; Parthsarathy, R.; Menon, V. Synth Met 1993, 55, 1165.
9. Brumlik, C. J.; Martin, C. R. J Am Chem Soc 1991, 113, 3174.
10. Huang, J.; Wan, M. J Polym Sci 1999, 37, 151.
11. Yongsheng Yang and Meixiang Wan J. Mater. Chem., 2002, 12, 897-901
12. Umari M H, Varadan V V and Varadan V K *Radio Sci.* 1991 26 1327-34
13. Varadan V K, Varadan V V and Lakhtakia A J. Wave-Material Interaction 1987 2 71-81
14. Guocai Sun, Kailun Yaoz, Zuli Liuy and Quanliang Huangy J. Phys. D: Appl. Phys. 31 (1998) 2109-2111.
15. M Schwientek, S. Plens and C. H. Hamann, J. Electroanal. Chem., 1999, 461, 94.
16. S. Pleus and M. Schwientek, Synth. Met., 1998, 95, 233.
17. Z. D. Chen, Y. Takei, B. A. DeoYe and T. Nagaoka, Analyst, 2000, 125, 2249.

(a) L.Mare, D. Diadier, G. Robert, G. Alain and R. Jean, J. Chem. Soc., Chem. Commun., 1988, 658; (b) Y. X. Zhou, B. Yu and G. Y. Zhu, Polymer, 1997, 38, 5493.

18. H. S. Lee and J. Hong, J. Chromatogr. A., 2000, 868, 189.

19. Z. D. Chen, A. Okimoto, T. Kiyonaga and T. Nagaoka, Anal.Chem., 1999, 71, 1834.
20. H. L. Guo, C. M. nobler and R. B. Kaner, Synth. Met., 1999, 101, 44.
21. G. C. Sun, K. L. Yao, H. X. Liao, Z. C. Niu and Z. L. Liu, Int.J. Electron., 2000, 87, 735.
22. L. A. P. Kane-Maguire, I. D. Norris and G. G. Wallace, Synth.Met., 1999, 101, 817.
23. D. Delabouglise and F. Garnier, Synth. Met., 1990, 39, 117.
24. M. Salmon, M. Saloma, G. Bidan and E. M. Genies, Electrochim.Acta, 1989, 34, 117.
25. J. C. Moutet, E. Saint-Aman, F. Tran-Van, P. Angibeaud and J. P. Utille, Adv. Mater., 1992, 4, 511.
26. [a] R. L. Elsenbaumer, H. Eckhardt, Z. Iqbal, J. Toth and R. H. Baughman, Mol. Cryst. Liq. Cryst., 1988, 917; [b] F. Chen, P. Akhtar, L. A. P. Kane-Maguire and G. G. Wallace, Aust. J. Chem., 1997, 50, 939.
27. D. Kotkar, V. Joshi and P. K. Ghosh, J. Chem. Soc., Chem.Commun., 1988, 917.
28. [a] M. Lemaire, D. Delabouglise, R. Garreau, A. Gay and J. Roncal, J. Chem. Soc., Chem. Commun., 1988, 658;[b] M. Lemaire, D. Delabouglise, R. Garreau and J. Roncal, Chim. Phys.-Chim. Biol., 1989, 86, 193.
29. M. Anderson, P. O. Ekeblad, T. Hjertberg, O. Wennestro¨m and O. Ingana¨s, Polymer, 1991, 32, 546.
30. S. A. Asharf, L. A. P. Kane-Maguire, M. R. Majidi, S. G. Pyne and G. G. Wallace, Polymer, 1997, 38, 2627.
31. M. R. Majidi, L. A. P. Kane-Maguire and G. G. Wallace, Aust.J. Chem., 1998, 51, 23.
32. E. V. Strounina, L. A. P. Kane-Maguire and G. G. Wallace, Synth.

Met., 1999, 106, 129.

33. D. Norris, L. A. P. Kane-Maguire, G. G. Wallace and L. H. C. Mattoso, Aust. J. Chem., 2000, 153, 89.
34. J. V. Barris, P. C. Innis, L. A. P. Kane-Maguire, I. D. Norris and G. G. Wallace, Synth. Met., 1997, 84, 181.
35. M. R. Majidi, L. A. P. Kane-Maguire and G. G. Wallace, Polymer, 1996, 37, 359.
36. V. Aboutanos, J. N. Barisci, L. A. P. Kane-Maguire and G. G. Wallace, Synth. Met., 1999, 106, 89.
37. P. C. Innis, I. D. Norris, L. A. P. Kane-Maguire and G. G. Wallace, Macromolecules, 1998, 31, 6521.
38. Feng Yan; Gi Xue J.Mater.Chem. 1999,9 3035-3039
39. E. Marie, R. Rothe, M. Antonietti, K. Landfester, Macromolecules 2003, *36*, 3967-3973
40. K. Landfester, R. Montenegro, U. Scherf, R. Güntner, U. Asawapirom, S. Patil, T. Kietzke, D. Neher, Adv. Mater. 2002, *14*, 651-655.
41. T. Piok, S. Gamerith, C. Gadermaier, U. Scherf, K. Landfester, E. J. W. List,, Adv. Mater. 2003, *15*, 800-804.
42. T. Kietzke, D. Neher, K. Landfester, R. Montenegro, R. Güntner, U. Scherf, Nature Materials
43. A.J.Epstein et al in Proceedings of the NATO Advanced research workshop of intrinsically. Cond,Pol,Burlington 1992 Ed. M. Aldissi pp 165-178, Kluwer, Dordecht 1993

Chapter 5

Studies On Polyaniline Composites

5.1 INTRODUCTION

Intrinsically conducting polymers (ICPs) and their blends with thermoplastics are very promising for applications in electromagnetic interference shielding (EMI). They can have relatively high conductivities and permittivities and these properties can be tuned easily from insulating to conducting states through chemical processes. Compared to metals, ICPs are light, flexible and they can not only reflect but also absorb electromagnetic radiations. Polyaniline (PAni) has attracted considerable interest as a conducting polymer. It is studied extensively for a variety of applications, including rechargeable batteries[1] EMI shielding[2], and biosensors[3], but PAni is mechanically weak and its processability is poor. It degrades before melting, is insoluble in common organic solvents, soluble only in concentrated sulfuric acid[4] under the specific condition, and also limitedly soluble in organic solvents like *N*-

methylpyrrodidone and tetrahydrofuran[5]. In order to circumvent these problems, many research groups[6,7,8] have utilized the method of synthesizing composites and copolymers. A new conducting graft copolymer PVC-g-PAni, that is processable and having desirable mechanical properties, is accessible by electrochemical method using a precursor polymer, poly (vinyl 1,4-phenylenediamine)(PVPD). The electrochemical properties of graft copolymer are compared with those of PVC/PAni composites. PVC is used for the backbone polymer because it can provide good mechanical properties and has reactive chlorine atoms for graft sites even though their reactivity is low. Polyaniline composites with fullerene (C_{60}) are of both scientific and technological interest. The area of applications includes various types of devices such as photodiodes, solar cells, photodetectors, sensors, etc. The formation of PAni-C_{60} composites faces the problem to disperse and mix both components to a molecular level because their solubility is limited. Blends and composites exhibit higher thermal stability than parent polymer[9]. A completely soluble polyaniline-multi-wall carbon nanotube (CNT-PAni) composite with significantly enhanced conductivity, improved thermal stability, and luminescent behaviour, has been synthesized. The presence of straight multi-wall carbon nanotubes during the polymerization of aniline induces the formation of a more planar conformation of polyaniline which acts as coating layer for the carbon nanotubes and leads to favourable interaction between the constituents[10]. Discs of poly (aniline)-silver-polymer electrolyte particulate composites exhibit rapid and reversible changes in their microwave impedance when small electric fields are applied across them in a coaxial line test set in a resonant condition[11]. A novel type of smart material in which microwave reflectivity is changed by the application of a low electric field (<10 V cm-1) was recently reported[12] . Composites of randomly mixed polyaniline and silver particles within a poly (ethylene oxide) (PEO) based polymer electrolyte[13] containing a silver salt were shown to respond to changes in applied field when their microwave reflectivity's were examined. Interpenetrating organic polymer composites consisting of two conducting polymers have been successfully prepared by sequential electropolymerization of the parent monomers:aniline and 3,4-ethylenedioxythiophene[14]. The electropolymerization of poly(3,4-ethylenedioxythiophene) (PEDOT) and polyaniline (PAni) was carried out in acetonitrile solution.

Conducting polymer composites with some suitable composition of one or more insulating materials lead to desirable properties. These materials are especially important owing to their bridging role between the world of conducting polymers and that of nanoparticles. For application of conducting polymers, knowing how these conducting polymer composites will affect the behaviour in an electric field is a long-standing problem and of great importance. But very little is known about the dielectric properties of conducting polymer associated with the conducting mechanism. Dielectric spectroscopy has been found to be a valuable experimental tool for understanding the phenomenon of charge transport in conducting polymers. Low frequency conductivity and dielectric relaxation measurements especially have proven to be valuable in giving additional information on the conduction mechanism that d.c. conductivity measurement alone does not provide.

The first section of this chapter reports the preparation and dielectric properties of PAni composites with Polyvinyl chloride [PVC]. Only a preliminary line of work has been attempted. Measurements were carried out on pelletised samples of these composites by Cavity Perturbation technique. The S band [2GHz-4GHz] was used for the study of the pellet samples.

PART I

5.2 POLYANILINE : POLYVINYL CHLORIDE COMPOSITES

5.2.1 INTRODUCTION

Among the conducting polymers, polyaniline (PAni) has received much attention because of its unique reversible proton doping, high electrical conductivity and ease of bulk preparation. However, to make polyaniline technologically viable, processability and thermal stability of polymer have to be improved. Copolymerization may be a simple and convenient method to accomplish this task.

Polyaniline is considered as one of the most promising candidate for the fabrication of conductive blends / composites with industrially important class of polymers[15]. The dc and ac conductivity of polyaniline / polyvinyl-alcohol blends[16] and polyaniline and zinc sulfide composites were studied in the microwave field[17]. There are a number of papers dealing with this composite. Banerjee and Mandal[18,19] have prepared blends of HCl doped polyaniline nanoparticles with polyvinyl chloride. Polyaniline-PVC composite films prepared by solution blending in the presence of phosphoric acid and HCl as the dopants were also reported[20,21]. A processable polyaniline / polyvinyl chloride composite was prepared by dispersing polyaniline in PVC matrix by mechanical mixing and then compression moulding in a hot press[22]. The electrochromic behaviour of polyaniline-PVC composite films with structural changes in polyaniline, using FTIR studies were also reported[23]. Kaiser et al[24] have recently reported the conductivity and thermopower data for polyaniline blends with polyvinyl chloride, which showed an increase in conductivity at lower temperature.

5.2.2 EXPERIMENTAL SECTION

- ***Preparation of PAni : PVC composites [$HClO_4$- in situ doped]***

Chemical oxidative polymerization of aniline is carried out using ammonium per sulphate as initiator in the presence of 1M $HClO_4$ and emulsion grade polyvinyl chloride. The polymerization is carried out for about 4 h at room temperature. It is then filtered, washed and dried in oven (at 50-60 °C for 6h). Different proportion of PAni: PVC composites, say, 4:1, 2:1, 1:1, 1:1.5, 1:2 and 1:2.5 are prepared using the above procedure and the microwave properties are measured.

5.2.3 RESULTS AND DISCUSSIONS

5.2.3.1 Variation of dielectric properties with composition of PAni :PVC

1. Dielectric Loss and Conductivity:

The dielectric loss and conductivity for different proportions of the composites in pellet form are plotted in Figure 5.1 and 5.2 respectively.

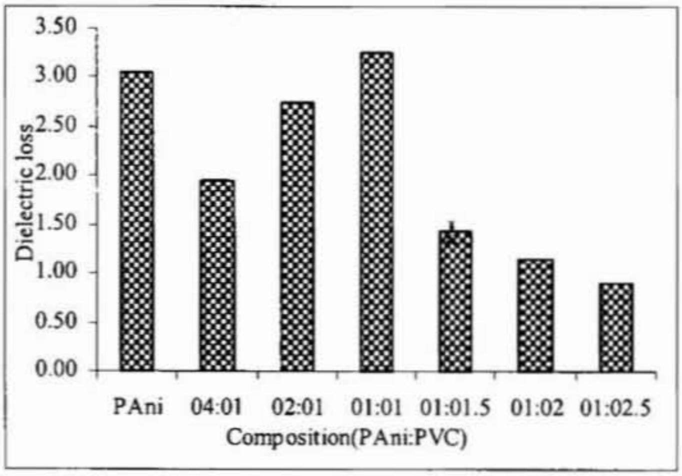


Figure 5.1: Variation of Dielectric loss with composition of PAni :PVC at 2.97 GHz

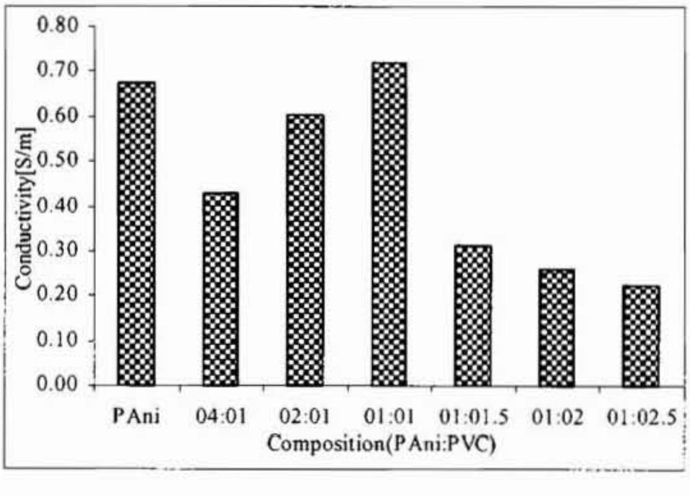


Figure 5.2: Variation of Conductivity with composition of PAni: PVC at 2.97 GHz

It is found that the introduction of PVC first decreases the dielectric loss and then increases to a maximum value when compared to PAni alone as shown in the figure 5.1.On adding a non-conducting material to a conducting matrix, the concentration of the conducting polymer decreases and it reduces the dipolar polarization, thereby it reduces the dielectric loss and conductivity. But it is clear from the graphs that higher quantity of PVC increases the dielectric loss and conductivity of the virgin conducting Polyaniline.

A maximum value is given by the 1:1 proportion as shown in the figures. In heterogeneous dielectrics, the accumulation of virtual charge at the interface of two media having different dielectric constants ε_1 and ε_2 and conductivities σ_1 & σ_2 respectively, interfacial polarization takes place[25] In the case of Polyaniline-PVC composite which consist of two phases, a charge build up can occur at the macroscopic interface as a result of the differences in the conductivity and dielectric constant of the materials. This accumulation of charge then leads to field distortions and dielectric loss. This interfacial loss depends on the quantity of weakly polar material present as well as on the geometrical shape of its dispersion[26]. It is clear that the PVC as a second phase in Polyaniline with a different dielectric constant and conductivity contributes to the interfacial polarization and thereby a high dielectric loss is observed for the composite. The quantity and geometry of the PVC at 1:1 proportion is more favorable for higher interfacial polarization. This may be the reason why maximum dielectric loss and conductivity is shown by the 1:1composition of PAni: PVC composite.

2. Dielectric Constant:

It is clear from the graphs that the dielectric constant for Polyaniline alone is much higher when compared to the PAni: PVC composite. Incorporation of a non-polar or weakly polar material into a good dielectric material results in a decrease of dielectric constant[27]. It is clear from the figure that the dielectric constant decreases with increase in PVC content because of the presence of weakly polar PVC.

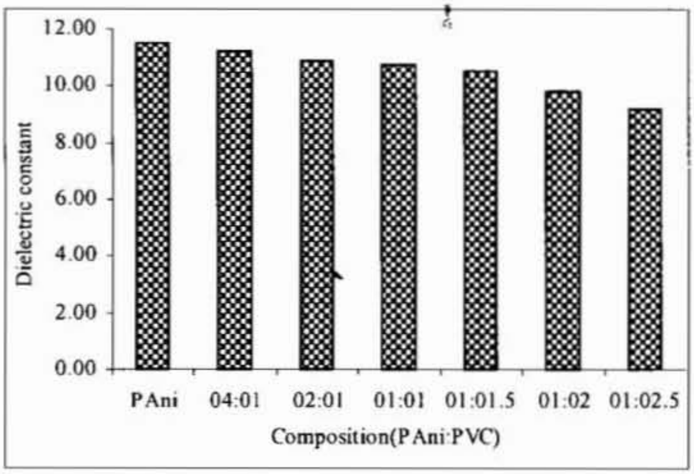


Figure 5.3: Variation of Dielectric constant with composition of PAni: PVC at 2.97 GHz

3. Loss Tangent

Figure 5.4 shows the variation of loss tangent for different proportions of composites. The loss tangent is directly related to the dielectric loss and hence the loss tangent is higher for 1:1proportion as expected.

4. Dielectric heating coefficient

Figure 5.5 shows the variation of dielectric heating coefficient of different proportions of PAni: PVC composites. It is clear from the figures that the dielectric heating coefficient decreases with increase in PVC content. The figure shows that the dielectric heating coefficient is minimum for 1:1 (PAni: PVC) proportion as expected.

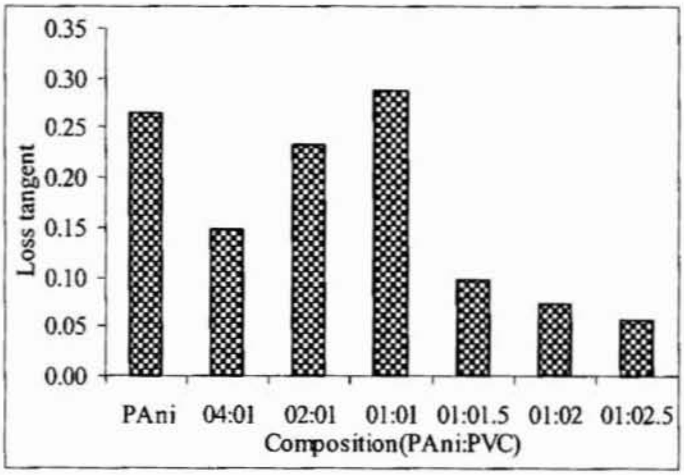


Figure 5.4: Variation of Loss tangent with composition of PAni: PVC at 2.97 GHz

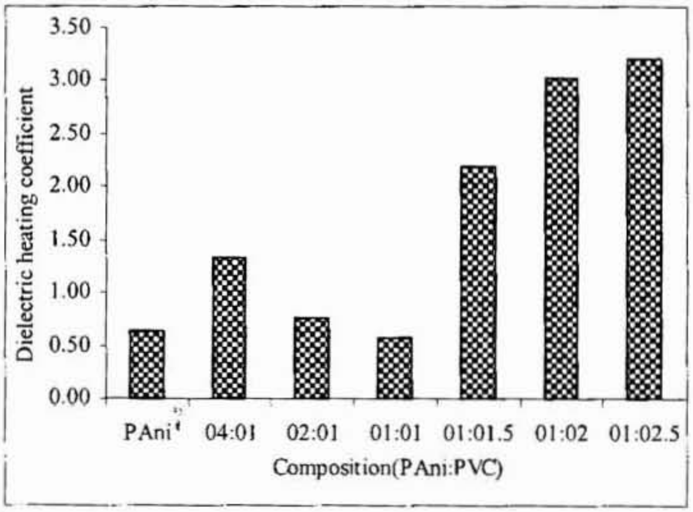


Figure 5.5: Variation of Dielectric heating coefficient with composition of PAni:PVC at 2.97 GHz

5. Absorption coefficient and penetration depth

It is clear from the graph 5.6 that the absorption coefficient is higher for 1:1 proportion since the absorption coefficient is a direct function of dielectric loss. Penetration depth or Skin depth is inversely related to the dielectric loss and hence it is lower for 1:1 composition as shown in the figure 5.7.

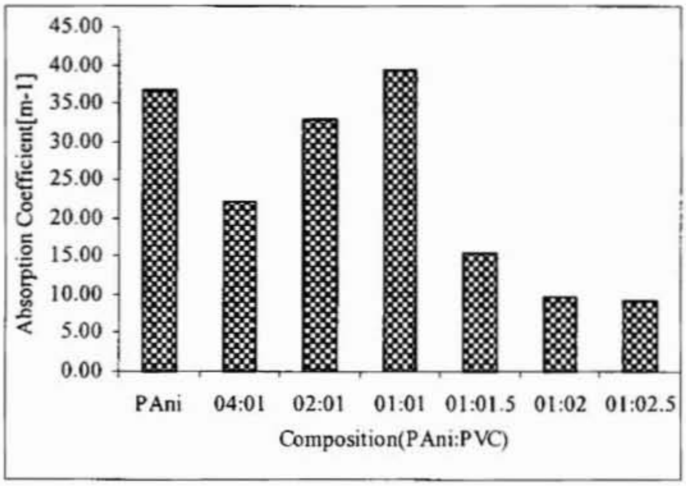


Figure 5.6: Variation of Absorption coefficient with composition of PAni: PVC at 2.97 GHz

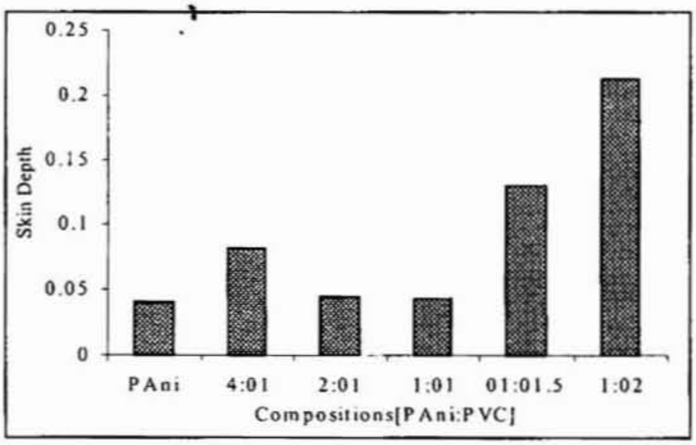


Figure 5.7: Variation of Skin Depth with composition of PAni : PVC at 2.97 GHz

PART II

5.3 POLYANILINE: SILICA COMPOSITES

5.3.1 INTRODUCTION

Preparation of Polyaniline/silica, poly-*o*-toluidine/silica and poly-2-chloroaniline/silica composites have been reported under a variety of synthetic conditions by polymerizing the respective monomers in the presence of silica prepared *in situ* from an aqueous sodium silicate solution. A wide range of experimental techniques including elemental analysis for silica content, density, infrared spectroscopy and sedimentometry for particle size determination has characterized the composites, thus synthesized. When used as column material in the IGC experiments, synthesized composites have been found to be capable of separating the alkanes (C_5–C_9) from their mixture. Recent studies have demonstrated that ER fluids containing anhydrous non-conducting polymers[28] or organic-inorganic composite particles[29-32] had not exhibited an appreciable ER effect. The polarizability of these materials is high and no surface activator is needed. Among them, polyaniline (PAni) is a polymer that is easy to prepare by the oxidative polymerization of aniline. Adjusting the degree of protonation can control its conductivity and dielectric properties. The electrorheology of silica particles coated with protonated polyaniline or polyaniline base in silicone oil has been studied. The behaviour of suspensions has been compared with those of bare silica particles and polyaniline base powder. The electrorheological performance of these systems has been compared and reported in connection with the polarization characteristics resulting from the frequency spectra of permittivity and dielectric loss of suspensions and from the particle dipole coefficient.

In this section of study, we have attempted a preliminary line of work on PAni:Silica composites. The dielectric response in the S band of the microwave region is studied for the composites prepared with different grades of commercial silica[U-Sil], ultrafine silica [VN3] and precipitated silica [PPSi]. A comparison in properties of the three types of composite matrices have been evaluated

5.3.2 EXPERIMENTAL

[i] Preparation of Pani:Silica composites

Chemical oxidative polymerization of aniline is carried out using ammonium per sulphate as initiator in the presence of silica. Parallel reactions are carried out for all the three grades of silica abbreviated as U-Sil, VN3, and PPsi. The polymerization is carried out for about 4h at room temperature. It is then filtered, washed and dried in oven (at 50-60^{0}C for 6 hrs). Different amounts of silica are added to study the resultant variation in properties. They are prepared using the above procedure and the microwave properties are measured using the resonant cavity technique.

5.3.3 RESULTS AND DISCUSSIONS

5.3.3.1 Variation of dielectric properties with composition of PAni: Silica

1. Dielectric Loss and Conductivity:

The dielectric loss and conductivity of different proportions of composites in pellet form is plotted in figure 5.8 and figure 5.9 respectively. It is very interesting that the dielectric loss and conductivity of composite increases with increase in silica content, irrespective of the nature of the silica.

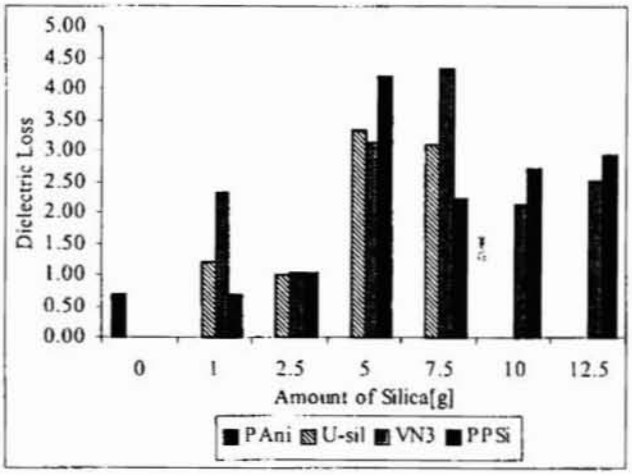


Figure 5.8: Variation of Dielectric Loss with composition of PAni:silica at 2.97 GHz

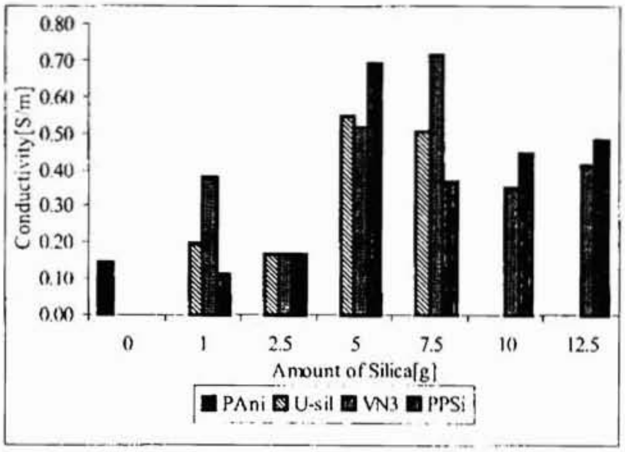


Figure 5.9: Variation of Conductivity with composition of PAni :silica at 2.97 GHz

The conductivity of the base conducting polymer (Polyaniline) increases on adding silica and it reaches a maximum for 1:1.5 proportion in all cases as shown in the figure. In the case of Polyaniline-Silica composites, which consist of two phases, a charge build up can occur at the macroscopic interface as a result of the differences in the conductivity and dielectric constant of the materials. This accumulation of charge then leads to field distortions and dielectric loss. The quantity and geometry of the Silica at 1:1.5 proportion is more favourable for higher interfacial polarization. This may be the reason why maximum dielectric loss and conductivity is shown by the 1:1.5 composition of PAni: Silica composites. Among all the silica, the VN_3 shows a uniform spherical shape [Figure 5.10] and as the VN_3 silica uniformly distributes in the Polyaniline matrix and the dielectric properties are improved.

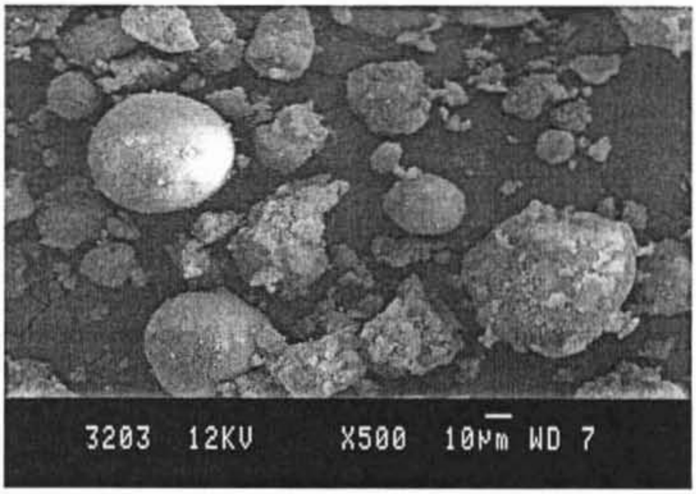


Figure 5.10: Scanning Electron Micrograph of VN3

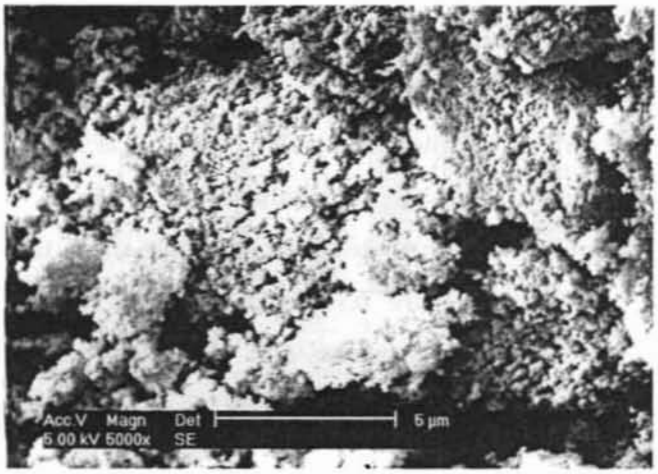


Figure 5.11: Scanning Electron Micrograph of PAni: VN3

2. Dielectric constant

The variation of dielectric constant with different proportions in pellet form is plotted in figure 5.12. It is clear from the graphs that the dielectric constant for Polyaniline alone is much higher when compared to the PAni: Silica composite. It is clear from the figure that the dielectric constant decreases with increase in Silica content because of the presence of weakly polar Silica.

3. Dielectric Heating Coefficient

Figure 5.13 shows the variation of dielectric heating coefficient of different proportions of PAni: Silica composites. It is clear from the figures that the dielectric heating coefficient decreases with increase in Silica content and is minimum for 1:1.5 (PAni:Silica) proportion. The low value of dielectric heating coefficient is important for dielectric heating application. The high dielectric loss for the 1:1.5 composition leads to low heating coefficient and it is a minimum for VN3 composition as expected.

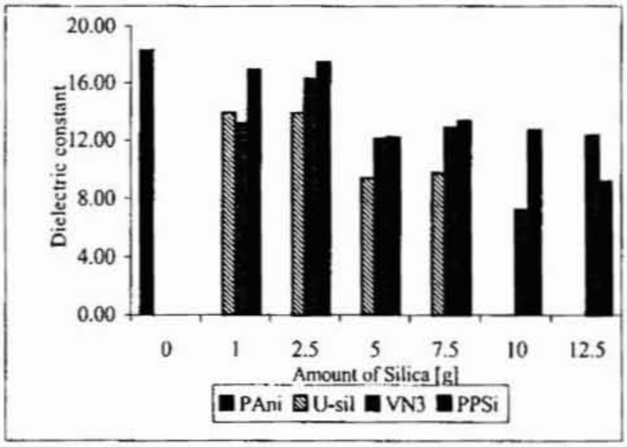


Figure 5.12: Variation of Dielectric constant with composition of PAni:silica at 2.97 GHz

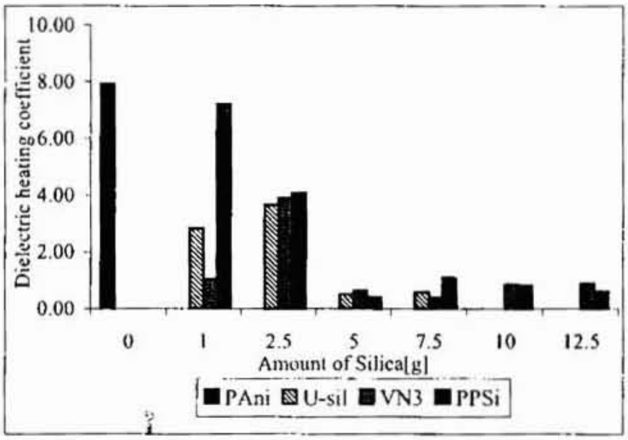


Figure 5.13: Variation of Dielectric heating coefficient with composition of PAni:silica at 2.97 GHz

3. Loss Tangent

Figure 5.14 shows the variation of loss tangent for different proportions of the composite. The loss tangent is directly related to the dielectric loss and hence the loss tangent is higher for 1:1.5 proportion of VN_3 as expected.

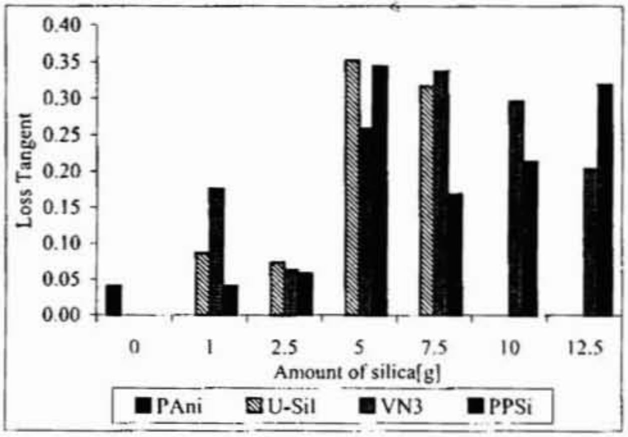


Figure 5.14: Variation of Loss tangent with composition of PAni: silica at 2.97 GHz

4. Absorption Coefficient and Skin depth:

Figure 5.15 and 5.16 shows the absorption coefficient and skin depth of silica composites respectively. It is clear that the absorption coefficient is higher for 1:1.5 proportion and the skin depth is lower for 1:1.5 composition. The absorption coefficient is a direct function of dielectric loss and skin depth is inversely related to the dielectric loss. This property could be useful for shielding electromagnetic radiations.

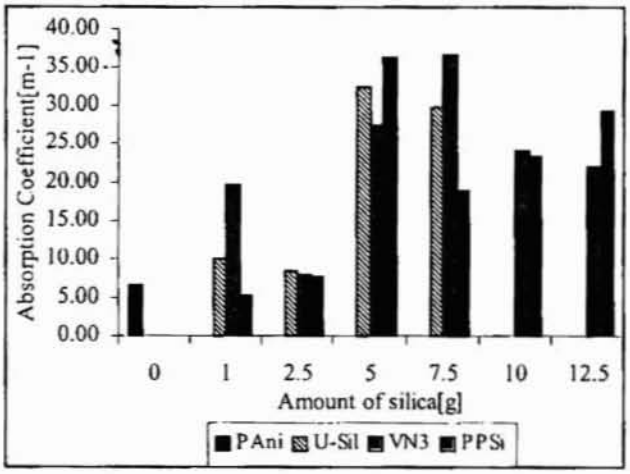


Figure 5.15: Variation of Absorption coefficient with composition of PAni:silica at 2.97 GHz

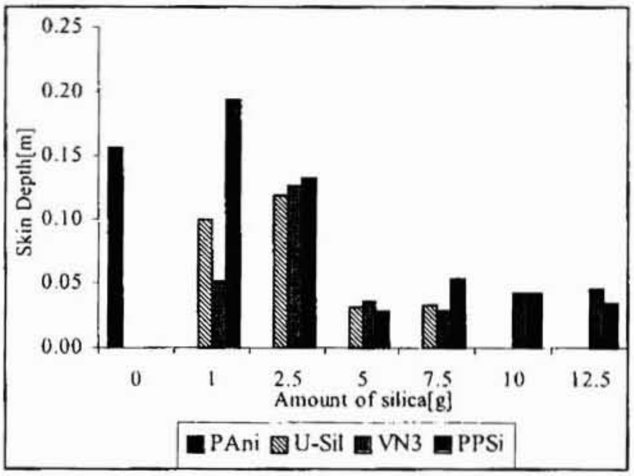


Figure 5.16: Variation of Skin depth with composition of PAni:silica at 2.97 GHz

5.4. CONCLUSIONS

- PAni :PVC composites prepared by in situ polymerization using $HClO_4$ dopant shows high conductivity and dielectric loss when compared to PAni [$HClO_4$]
- The dielectric loss, conductivity, absorption coefficient etc are found to increase with increase in PVC loading up to 1:1 proportion.
- The dielectric heating coefficient and skin depth are found to decrease with increase in PVC loading and it shows a minimum value for 1:1 PAni:PVC composite
- Among the different types of silica composites, PAni:VN3 combination shows better dielectric response than the other two matrices.
- The conductivity and absorption coefficient is found to be maximum for 1:1.5 PAni: Silica composite.
- The dielectric heating coefficient and penetration depth or skin depth is found to be minimum for 1: 1.5 PAni :Silica composite.

5.5 REFERENCES

1. Genies, E. M., Hany, P., & Santier, C. (1988). A rechargeable battery of the type polyaniline/ propylene carbonate-lithium perchlorate/lithium-aluminum. J. Applied Electrochemistry, 18, 751-761.

2. Joo, J. & Epstein, A. J. (1994). Electromagnetic radiation shielding by intrinsically conducting polymers. Applied Physics Letters, 65, 2278-2280.

3. Bartlett, P. N. & Birkin, P. R. (1993). The application of conducting polymers in biosensors.Synthetic Metals, 61, 15-21.

4. Andreatta, A., Heeger, A. J., & Smith, P. (1990). Electrically conductive polyblend fibres of polyaniline and poly (p-phenylene terephthalamide). Polymer Communications, 31, 275-278.

5. Wang, S., Wang, F., & Ge, X. (1986). Polymerization of substituted aniline and characterization of the polymers obtained. Synthetic Metals, 16, 99-104.

6. Park, Y. H., Choi, S. H., Song, S. K., &. Miyata, S. (1992). Synthesis of highly conducting nylon6 composites and their electrical properties. J. Applied Polymer Science, 45, 843-852.

7. Zilberman, M., Titleman, G. I., Siegmann, A., Habe, Y., Naskis, M., & Alperstein, D. (1997). Conductive blends of thermally dodecylbenzene sulfonic acid-doped polyaniline with thermoplastic polymers. J. Applied Polymer Science, 66, 243-253.

8. Schemid, A. L., Lira, L. M., & Cordoba de Torresi, S. I. (2002). On the electrochemical and spectroscopic properties of a soluble polyaniline parent copolymer. Electrochimica Acta, 47, 2005-2011.

9. Sapurina, A. Gribanov, M. Mokeev, V. Zgonnik

10. R Sainz, A M Benito, M TMartýnez, J FGalindo J Sotres AMBaro B CorrazeO Chauvet A B Dalton RH Baughman andW K Maser Nanotechnology 16 (2005) 150-154

11. A Barnes, A Despotakis, T C P Wong, A P Anderson,B Chambers and P V Wright Smart Mater. Struct. 7 (1998) 752-758.

12. Barnes A, Despotakis A, Wright P V, Wong T C P,Chambers B and Anderson A P Electron. Lett 1996 32 358-9

13. Wright P V Br. Polym. 1975 J. 7 319

14. H. Randriamahazaka, V. Noël, S. Guillerez, C.Chevrot, *J. Electroanal. Chem.* (in press).

15. H. Han, T. Matobe, Y. E. Whang S. Miyata, Synth. Metal, **45**, 261,(1991)

16. P.Banerjee and B.M.Mandal ., Macromolecules, 1995,**28**,3940.

17. C.K.Subramaniam, A.B.Kaiser, P.W. Gilberd, and B.Wessling, J. polymer sci.,polymer phys., 1993,**31**,1425.

18. A.Pron, J.E. Osterholm, P.Smith, A.J.Heeger, J.Laska and M.Zagorska.,Synth.Met., 1993,**57**,3520.

19. M.Thangarathinavelu, A.K.Tripathi, T.C. Goel and I.K.Varma, J.Appl.Polym.Sci., 1994,**51**,1347.

20. L.W.Shacklette, C.C.Han and M.H.Luly., Synth.Met., 1993,57,3532.

21. L.Terlemezyan, M.Mihailov and B.Ivanova., Polym.Bull., 1992,**29**,283.

22. A.B.Kaiser, C.K.Subramaniam, P.W.Gilberd and B.Wessling., Synth.Met. 1995,**69**,197.

23. J.C.Maxwell, Electricity and Magnetism, Oxford University Press, Oxford (1892)

24. Anand Jayasree, Srinivasan palaniappan and D, N. Sathyanarayana, Prog.Polym.Sci., **23**,993-1018,1998

25. R.W.Sillars, IEE Journal, 1937,80,371.

26. N.G.McCrum,B.Ee. Read, G.Williams,Anelastic Dielectric Effectsb in Polymer solids, John Wiley & Sons Ltd., London, 1967

27. R.J.Maccallum, C.A. Vincent, Polymer Electrolyte Reviews II, Elsevier Applied Science Publuishers Ltd, London and New York, 1987,Ch.2.

Chapter 6

Comparative and Applications Study

PART I

6.1 A COMPARATIVE STUDY

Conducting polymers have many potential applications in the microelectronics industry since they have been proved to be excellent substitutes for metals and semiconductors. Conducting polymers are effective discharge layers as well as conducting resists in electron beam lithography. They find applications in metallization of plated through-holes for printed circuit board technology, provide excellent electrostatic discharge protection for packages and housings of electronic equipment, provide excellent corrosion protection for metals, and may have applications in electromagnetic interference shielding.

Among a large variety of conducting polymers, Polyaniline is preferred for many applications since it offers a number of advantages due to its extensive chemical versatility. Polyaniline (PAni) is prepared by the oxidative polymerization of aniline, which is an easy one-step synthesis involving inexpensive raw materials. Also the environmental stability of PAni appears to be good compared to a number of other conducting polymers. For this reason, it is one of the most potentially useful conducting polymers. The use of polyaniline films in microelectronics, especially microwave-printed circuits, requires the study of their electric behavior at high frequencies. The two fundamental properties of a conductor at high frequencies are its bulk conductivity and skin depth. Since the quality of conducting films for microwave applications (patch antenna, filters, oscillators, etc.) depends heavily on their conductivity and smooth surface, accurate values for microwave conductivity and permittivity are very important for the efficient utilization of these films. In highly conductive polymers, conductivity does not depend on frequency, at least up to 12 GHz.

Microwave techniques for measuring the dielectric properties (permittivity, conductivity, etc.) of insulator and semiconductor materials are well known and have been used for a long time, whereas microwave investigation of high super conducting materials is still a challenge.

In this chapter, a concise comparison of the dielectric properties of a few conducting matrices viz. Different forms of Polyaniline [PAni] is proposed to be given. Various properties like dielectric constant, conductivity, dielectric loss, heating coefficient, and absorption coefficient is measured using the resonant cavity technique.

6.1.1 *Preparation*

Conducting polyaniline in the doped state (using inorganic and organic) and undoped state were prepared as explained in chapter 3. The preparation of polyaniline with codopants and microemulsions are explained in chapter 4. Preparation of Poly aniline and its SIPN with PVC is same as explained in chapter 5.

6.1.2 RESULTS AND DISCUSSIONS

The matrices selected for the study are

PAni [undoped]	**A**
PAni: CSA: Glu	**B**
PAni: PVC [$HClO_4$]	**C**
PAni [HClO4]	**D**
PAni [2.5% émulsion]	**E**
PAni: NSA: Glu	**F**
PAni: CSA	**G**

1. Dielectric Loss (ε″) and conductivity (σ)

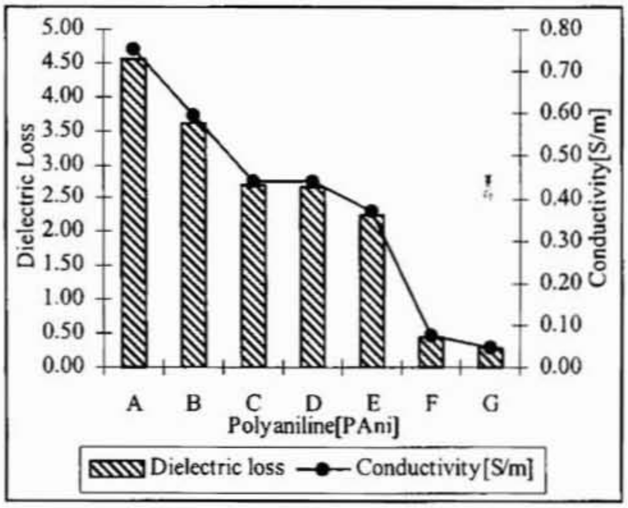


Figure 6.1: Variation of dielectric loss and conductivity with different forms of PAni

Figure 6.1 shows dielectric loss and conductivity of Polyaniline samples prepared under different conditions. Undoped Polyaniline state shows higher dielectric loss and conductivity. When Polyaniline is prepared in the undoped state, the ratio of amount of head to head to arrangement to that of head to tail arrangement is high compared to that prepared in the doped state. Hence two phases generated within the Polyaniline matrix itself leads to interfacial polarization. It is clear from the XRD analysis that undoped PAni give two peaks, one broad [at 2θ = 20°] and the one narrow [at 2θ = 25°], which indicates the presence of amorphous and crystalline regions in the polymer chain. It has been demonstrated that the ratio of half-width to height [HW/H] of X-ray diffraction peak reflects the order of the polymer backbone; the smaller the value of HW/H the higher the order. Even though, the crystalline portion decreases the dipolar polarization, it enhance the interfacial polarization and therefore in undoped PAni a combined effect of electronic polarization which is usual in non polar materials, and interfacial polarization occurs. In the case of CSA-Glucose-PAni, which holds the second position, the smaller grain size leads to better dipole orientation in the microwave field. It is clear from the XRD data that the CSA-Glucose system is more amorphous in nature. In the case of Polyaniline doped with $HClO_4$, the crystallinity increased, compared to CSA-codopant sample. When the crystallinity increases, the number of dipoles per unit volume decreases which decreases the dielectric loss.

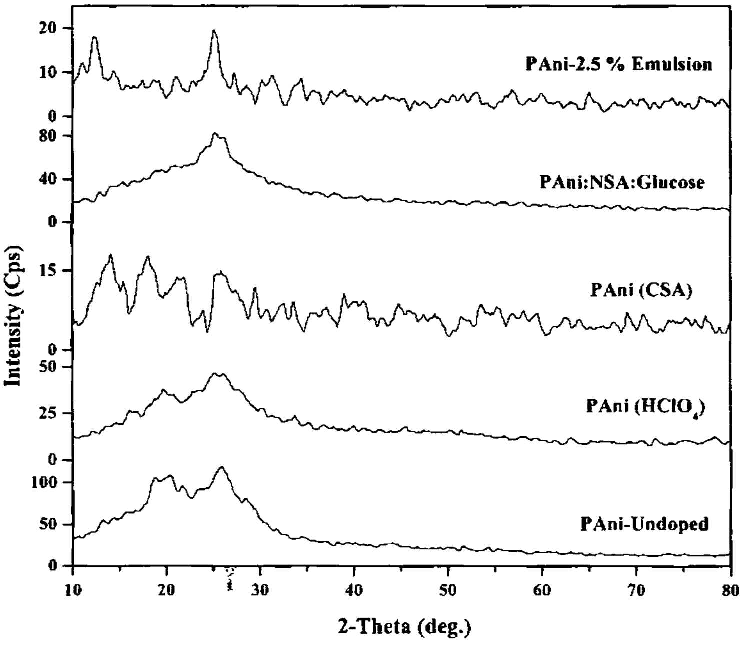


Figure 6.2 : Comparison of the X-ray diffraction patterns of selected Polyanilines

In the case of emulsion polymerized and NSA doped samples, the crystallinity further increased as is evident from the XRD pattern [Figure 6.2].

Since conductivity is directly related to the dielectric loss and hence the conductivity values follow the same trend as that of dielectric loss, i.e. it follows the order:

PAni [undoped]>PAni: CSA: Glu>PAni: PVC [$HClO_4$]>PAni [$HClO_4$]> PAni [2.5% émulsion]>PAni: NSA: Glu>PAni: CSA

2. Dielectric constant:

The dielectric constant is found to be highest for polyaniline doped with NSA-Glucose-PAni [Figure 6.3] and the trend is as follows: **PAni: NSA: Glu > PAni: CSA > PAni [2.5% emulsion] > PAni: CSA: Glu > PAni [undoped] > PAni: PVC [$HClO_4$]>PAni [$HClO_4$].** The dielectric constant is due to the accumulation of polar charges at the interface of the molecule.

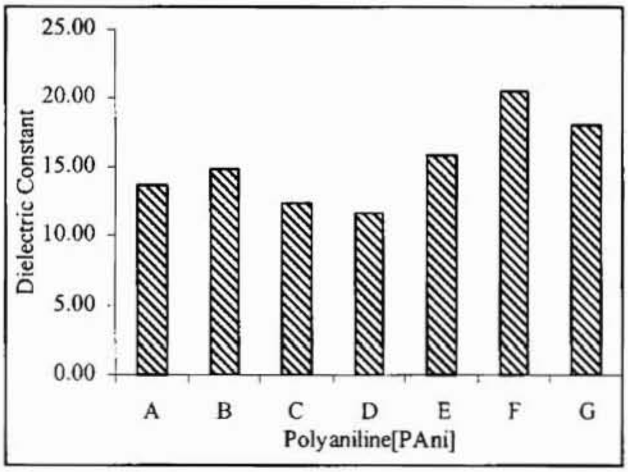


Figure 6.3 Variation of dielectric constant with different forms of PAni

3. Dielectric heating coefficient (J) and loss tangent (tan δ)

The dielectric heating coefficient is lower for undoped PAni. The dielectric heating coefficient is defined as $J = 1/\varepsilon_r \tan\delta$. The loss tangent tan δ is directly related to the dielectric loss and inversely related to the dielectric constant and therefore the heating coefficient is dependent on these factors. The lower the J value the better will be the material for dielectric heating applications.

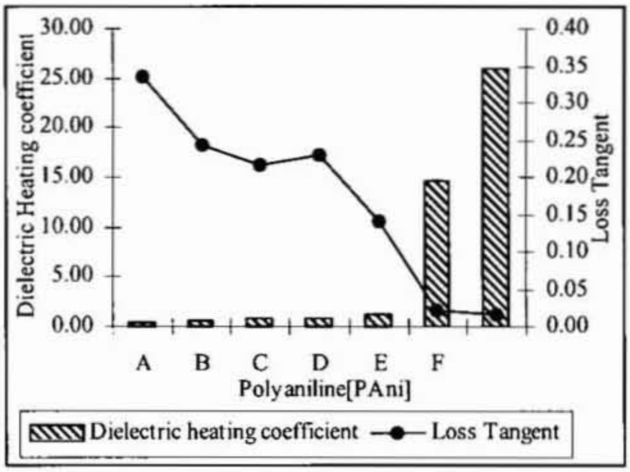


Figure 6.4 Variation of dielectric heating coefficient and loss tangent with different forms of PAni

The loss tangent follows the order **PAni [undoped]<PAni: CSA: Glu<PAni: PVC [HClO4]<PAni [HClO4]<PAni [2.5% émulsion]<PAni: NSA: Glu<PAni: CSA** and the dielectric heating coefficient follows the reverse order with PAni [undoped] showing the minimum dielectric heating coefficient and PAni[CSA] showing the maximum dielectric heating coefficient.

4. Absorption Coefficient and Skin Depth

It is very important to study the absorption coefficient and penetration depth for applications like electro magnetic interference (EMI) shielding. The absorption coefficient is dependent on the dielectric loss factor and is inversely related to the refractive index.

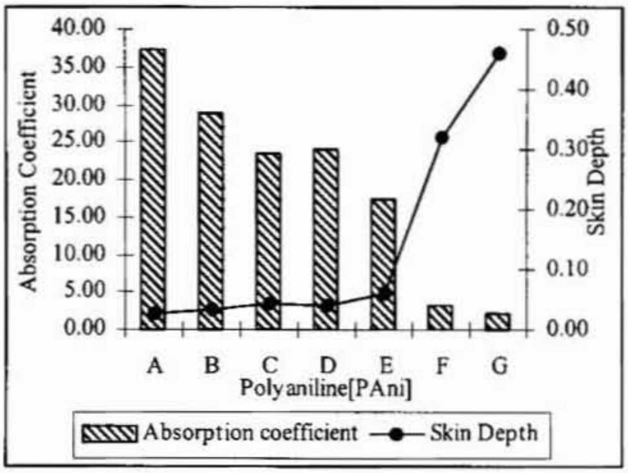


Figure 6.5. Variation of absorption coefficient and Skin depth with different forms of PAni

For highly lossy materials, the absorption coefficient is very high and the skin depth (the factor indicating the penetration of wave in to material) is minimum. Polyaniline ion in the undoped state shows a high dielectric loss and hence high absorption coefficient as shown in the figure 6.5. The variation of absorption coefficient is in the order **PAni [undoped]>PAni: CSA: Glu>PAni: PVC [HClO4]>PAni [HClO4]>PAni [2.5% emulsion]>PAni: NSA: Glu>PAni: CSA**

The skin depth of undoped Polyaniline is lower when compared to other polymers and it follows the reverse order.

PART II

6.2 APPLICATIONS STUDY

Microwave radiation spans the 300 MHz to 300 GHz frequency range of the electromagnetic spectrum. In terms of the frequency band, it is from the UHF band (0.3-to-1 GHz) to the sub millimeter band (>300GHz). Each band has its own specific applications. Out of these, the so-called 'S' band (2- 4 GHz) finds itself useful in 'Industrial, Scientific and Medical' (ISM) applications. These deal with the high power applications such as heating of materials and low power applications such as active sensors: -related to the measurement of attenuation, phase shift or delay of microwaves interacting with various materials, and passive sensors: -related to the measurement of thermal noise emitted or received by matter leading to IR thermography.

The ISM applications of microwaves are based on the interaction between microwaves and different kinds of materials. Some of the microwave materials used in the ISM applications are: Ceramics, polymers, crystals, ferrites, meta-materials and biomaterials. The study of dielectric properties of these materials in the ISM field is thus of prime concern.

The properties of dielectric materials in microwave field are usually described by their relative complex permittivity (ε), which is frequency dependent. Other important parameters are refractive index (μ), attenuation constant (α), phase shift constant (β) and conductivity (σ), which are derived from the complex permittivity

From the dielectric studies of Polyanilines in the field, it is observed that the dielectric constant of PAni [undoped] shows a variation with change in applied electric field. This inherent property of the material can be utilized favorably to shift the beam [electromagnetic radiation] from it normal path. When the strength of the applied field is changed, the dielectric constant of the material changes as a result of which the velocity of the radiation propagating through it changes and results in a phase shift. The ability to shift the phase angle causes the beam to be steered or deflected from its normal path. This property is extremely useful and advantageous due to the lack of heavy machinery involved in mechanical beam steering apparatus.

Few representative matrices described in thesis have been investigated for the beam steering property. Matrices such as PAni [undoped]; PAni [doped forms] show a beam shift. The experimental setup and the relevant results in this aspect are shown in the next section

Study of Material Loaded Dielectric Antenna

An antenna is constructed by using Perspex (permittivity 2.56) rod. The extreme ends are tapered for better matching with the medium as well as with the feed. Waveguide feed is employed for simplicity and is excited from a proper source via a co-axial-to-waveguide adapter. The waveguide has a cross section of 2.2 x 1 cm. The purpose is to test the electric field dependent nature of specially prepared conducting material by making it a part of the rod antenna. The material is loaded in the antenna at a length of maximum matching with the waveguide. The setup is shown below.

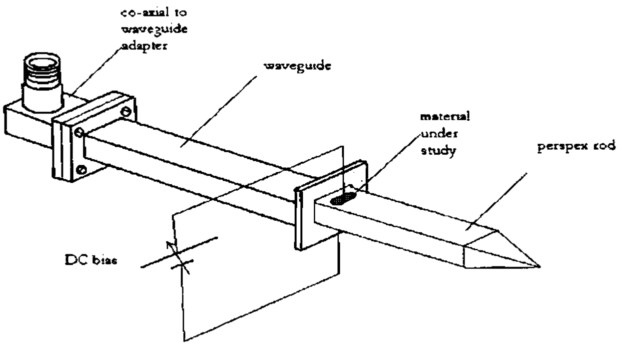


Figure 6.6: Dielectric material loaded antenna

The measurement setup consists of a microwave source, antenna, a turntable in which the above said rod antenna is placed, an X-Y recorder to record the radiation patterns and a dc power supply to vary the strength of the field.

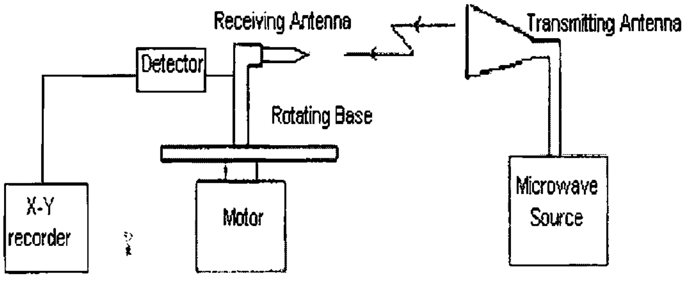


Figure 6.7: Experimental set up for beam steering property measurements

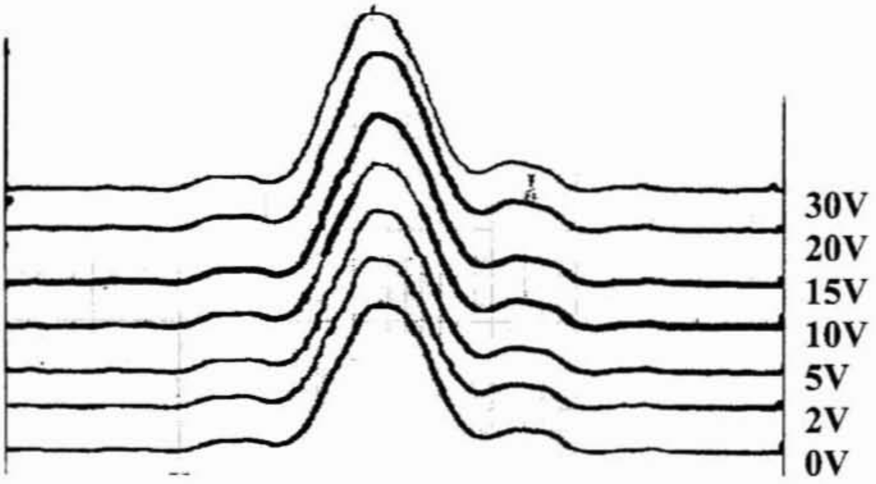


Figure:6.8: Radiation patterns observed for PAni[undoped]

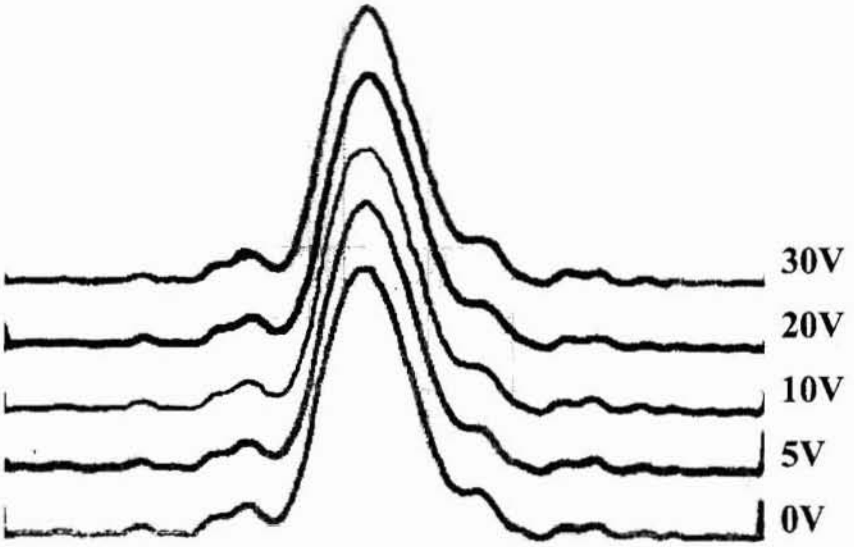


Figure:6.9 Radiation patterns observed for PAni [doped]

Figure 6.8 and 6.9 show the radiation patterns of the doped and undoped forms of Polyaniline. The samples exhibited beam steering with an angle shift of approximately 6° for the undoped sample. A shift of the order of 3° was obtained for a positive applied voltage. A similar result has been obtained for a negative applied voltage - a 3° shift is obtained for the doped sample.

Future studies are to be carried out by varying the effect of voltage variation and volume of the sample on the beam steering property of the material.

PART III

6.3 FUTURE OUTLOOK

- ⇨ To account for the dielectric response of conducting systems in the microwave and high frequency field, it may be necessary to have more information on the physical parameters of the molecules. A plausible tool to aid in a more refined view of things, is the dielectric spectroscopy of the material when perturbed under the influence of a high frequency field. The actual bond alterations can be studied in detail using the dielectric spectroscopic technique.
- ⇨ The structure property relationship has to be probed exhaustively to arrive at a suitable choice of matrix and dopant and synthesis conditions for possible microwave applications.
- ⇨ Manipulating the structural moieties of the polymer can vary the dielectric constant. High dielectric constant materials find many applications in microelectronics. Efforts in this line of work could lead to novel applications for these conducting polymers.

Chapter 7

Summary and Conclusions

Conductive materials based on polymers are being developed to provide lightweight flexible mouldable parts having static bleed off as well as EMI shielding properties. The optical properties, permittivity and permeability, of the conductive polymers can be varied over a wide range depending on synthetic and processing methods. The electrical energy in the conductive polymer arises from electrical currents induced by the electromagnetic field of the microwave interacting with electrons in the conductor. The imposition of an electrical field upon a polymer will cause a redistribution of any charges in the polymer provided they are mobile enough to respond in the time scale of the applied field. The synthesis of polyaniline in the undoped state and the development of conducting polyaniline microtubules and microemulsions which have been the major focus of our study, is found to be superior to conducting polymers used in electrical and microwave applications. The attractive features of conducting polymers studied are low cost, high microwave conductivity, high dielectric constant, high dielectric loss, high absorption coefficient and very low penetration depth and dielectric heating coefficient and good processability.

Chapter 1 gives a brief literature survey tracing the development of conducting polymers their strengths and weaknesses and hence leading to the scope and objective of the present investigation. The first part of the investigation was the preparation of PAni under different temperature and in the presence of different organic and inorganic dopants. The optimum parameters were then employed for the preparation of other systems such as PoT and PoAn.

The effect of various codopants like chiral sugars were evaluated and alternate preparation pathways such as emulsion polymerization was carried out to study the variability in properties. To improve the processability of the conducting polymer it was blended with Polyvinylchloride [PVC] and silica. The potential matrices were further evaluated in the high frequency field of .05-13 MHz using an impedance analyzer. Cavity perturbation Techniques allows the determination of microwave properties of pelletised conducting samples. Dielectric parameters like the dielectric loss, conductivity, constant, loss tangent, absorption coefficient and skin depth are measured over the S [2GHz-4GHz] band of the microwave region. A rectangular wave-guide was employed for the measurement. The sample was placed in a cavity resonator at the position of maximum electric field where the contribution of magnetic field for the perturbation is a minimum. The underlying principles and experimental set up has been outlined in Chapter 2 of the thesis.

The preparation of Polyaniline carried out at three different reaction temperatures with four separate inorganic acids as dopant is described in Chapter 3. The various dielectric properties were evaluated and $HClO_4$ doped samples are found to exhibit maximum dielectric loss and conductivity. The dielectric properties of polyaniline in the microwave frequencies are dependent on many chemical and physical parameters such as synthesis conditions, nature of dopant and the concentration of dopant. It is observed that Polyaniline prepared at room temperature gives better dielectric properties compared to the conventional low temperature and high temperature preparations. Among the inorganic acids used as dopant, 1M $HClO_4$ doped samples gave the best dielectric property. The dielectric effect of

Polyaniline in the undoped state was also studied. Undoped PAni was prepared under three different temperature conditions LT [low temperature], room temperature [RT] and high temperature [HT]. Samples prepared at RT and LT prepared samples showed comparable properties. A separate section deals with the effect of organic dopants such as NSA, CSA and TSA on the dielectric response of Polyaniline. NSA imparted a tubular morphology to the PAni formed whereas CSA doped PAni showed a higher conductivity and dielectric constant. The properties of PAni [Undoped] PAni [$HClO_4$] and PAni [CSA] have been compared and evaluated to give a better understanding of the dielectric behavior under the effect of various dopants and PAni in the undoped state. Among these three matrices, PAni in the undoped state gives the best result in the microwave field. The effect of preparation conditions and dopants of poly o-toluidine and polyo-anisidine on their dielectric properties has been investigated.

After the preparation conditions and dopants are optimized, the effect of morphological changes and preparation techniques on the dielectric parameters is studied. The effect of chiral sugars such as Glucose, Mannose and Sucrose as codopants with NSA is studied. The three different matrices showed tubular morphology owing to the presence of NSA as dopant, but better properties were observed for PAni:NSA:Glucose combination. The effect of CSA along with glucose as codopant was also studied. PAni:CSA:Glucose showed much better properties than PAni:CSA samples. PoT samples were also prepared in varying dopant codopant combination, but the SEM characterization did not show a tubular morphology, in spite of a better display of dielectric properties. The dielectric properties of all the matrices studied are supported by the IR spectroscopy, Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), XRD and SEM.

Polyaniline is most commonly prepared by chemical oxidative polymerization. An alternate route to Polyaniline preparation via an emulsion pathway is adopted and the samples have been analysed in the microwave and high frequency. A very uniform morphology with finer grain size is revealed in the SEM characterization.

Polyaniline PVC composites were prepared with $HClO_4$ dopant. The addition of a non-conductor 'PVC' can improve the dielectric properties of a conducting polymer in addition to improving the processability is taken in the solution form. It is also very peculiar that the PVC loading increases the dielectric loss, conductivity and absorption coefficient of the composites up to a particular proportion 1:1 PAni: PVC. The dielectric heating coefficient and penetration depth is the lowest for this particular proportion. Polyaniline: silica composites were prepared using three different grades on silica available. The dielectric parameters are evaluated based on the amount of silica added to the feed

Conducting polymers are being used for many microwave applications such as discharge layers and conducting resists in electron beam lithography. They also find applications in metallization of plated through-holes for printed circuit board technology, provide excellent electrostatic discharge protection for packages and housings of electronic equipment, provide excellent corrosion protection for metals, and may have applications in electromagnetic interference shielding.

Among a large variety of conducting polymers, polyaniline is preferred for many applications since it offers a number of advantages due to its extensive chemical versatility. Studies on the matrices showed a variation in dielectric constant with change in the frequency. These materials were then investigated for a possible microwave application such as in beam steering antenna. The experimental set up and findings are elucidated in the second section of chapter 7. PAni undoped and PAni doped showed a shift of 6° and 3° respectively.

LIST OF PUBLICATIONS:

1. Honey John, Rinku M.Thomas, K.T.Mathew, Rani Joseph, "Studies on the dielectric properties of poly o-toluidine and poly(o-toluidine-aniline) copolymer" *Journal of Applied polymer science* Vol. 92, Iss. 1, April 2004, 592-598.
2. Rinku M.Thomas, Honey John, K.T.Mathew, Rani Joseph Preparation of PPy:PVC and PPy:Silica Composites and comparison of their dielectric behaviour in microwave field *"Journal of Applied polymer science"(Accepted for publication)*
3. *R.M.Thomas, H.John, R.Joseph, K.T.Mathew "Studies On The Dielectric Properties Of Poly [O- Anisidine]/Poly Vinyl Chloride SIPN in comparison to Poly aniline /Poly vinyl chloride SIPN "*, ICMAT 2003, 2nd International Conference on Materials for Advanced Technologies & IUMARS-International conference in Asia , Symposium B, December 7-12,2003
4. H.John, R.M.Thomas, R.Joseph, K.T.Mathew "Effect Of Synthesis On The Dielectric Properties Of Polypyrrole And Its Composite With Poly Vinyl Chloride", *ICMAT 2003, 2nd International Conference on Materials for Advanced Technologies & IUMARS- International conference in Asia ,Symposium E, December 7-12, 2003*
5. R.M.Thomas, H.John, R.Joseph, K.T.Mathew "Preparation of PPy:PVC and PPy:Silica Composites and comparison of their dielectric behaviour in microwave field", APT-O4, International Seminar on Advances in Polymer Technology, January 16-17, 2004 (Kochi).
6. Honey John, Rinku M. Thomas, K.T.Mathew, Rani Joseph" Copnducting polyaniline-polyvinyl chloride for EMI shielding applications" *International seminar MACRO 2004, Thiruvananthapuram*
7. Rinku M. Thomas, Nisha V.S. Honey John, K.T.Mathew, Rani Joseph "Effect of particle size of polyaniline on microwave absorption" *International seminar MACRO* 2004 Thiruvananthapuram

LIST OF ABBREVIATIONS

%	Percentage
$(NH_4)_2S_2O_8$	Ammonium per sulfate
^0C	Degree Celsius
a.c.	Alternate current
ASTM	America society for testing and materials
cm	Centimeter
d.c.	Direct current
DSC	Differential scanning calorimetry
EMI	Electro magnetic interference
fs	Frequency
GHz	Giga hertz
gm	Gram
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
$HClO_4$	Perchloric acid
HNO_3	Nitric acid
CSA	Camphor sulfonic acid
TSA	Toluene sulfonic acid
NSA	Nahthalene sulfonic acid
Hz	Hertz
I_2	Iodine
IR	Infra red
J	Dielectric heating coefficient
KHz	Kilo hertz

LIST OF ABBREVIATIONS

%	Percentage
$(NH_4)_2S_2O_8$	Ammonium per sulfate
^{0}C	Degree Celsius
a.c.	Alternate current
ASTM	America society for testing and materials
cm	Centimeter
d.c.	Direct current
DSC	Differential scanning calorimetry
EMI	Electro magnetic interference
fs	Frequency
GHz	Giga hertz
gm	Gram
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
$HClO_4$	Perchloric acid
HNO_3	Nitric acid
CSA	Camphor sulfonic acid
TSA	Toluene sulfonic acid
NSA	Nahthalene sulfonic acid
Hz	Hertz
I_2	Iodine
IR	Infra red
J	Dielectric heating coefficient
KHz	Kilo hertz