STUDIES ON SELECTED CONDUCTING POLYMERS FOR MICROWAVE AND ELECTRICAL APPLICATIONS

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DEPARTMENT OF POLYMER SCIENCE AND RUBBER TECHNOLOGY
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Certificate

This is to certify that this thesis entitled “**Studies on selected conducting polymers for microwave and electrical applications**” is a report of the original work carried out by Smt. Honey John under our supervision and guidance in the Department of Polymer Science and Rubber Technology, Department of Electronics, Cochin University of Science and Technology, Cochin. No part of the work reported in this thesis has been presented for any other degree from any other institution.

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Honey John

"My heart praises the Lord, my soul is glad because of god my savior, for he has remembered me, his lowly servant! From now on all people will call me happy, because of the great things the Mighty God has done for me, His name is holy"
(Luke 1, 46-49)

My Father and My God, I come at the beginning of this meditation to ask that you will make my life like a watered garden. Let your fresh rivers run into my dead seas so that my whole being is revived day after day after day.

………… my husband Jose, for being my ray of life;
…… emmu and noyu, who always beckon me to smile

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Little did I realize, a few years ago, when I stepped in to this course of work that it would grow and develop into a completion of this manner. It was like threading back through every episode that I, have lived through these 3 years of research. It has demanded more discipline than I was capable of, but the rewards and experiences left me enriched.

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PREFACE

The electrical properties of polymers make up an inherently interdisciplinary topic, being closely associated, on the one hand, with the mechanical properties of polymers (polarization and relaxation) and, on the other hand, with the semi conductive properties (conduction and break down). In addition, unlike conventional technologies, which use these properties in its various applications like antistatic coatings, rechargeable batteries, sensors, electrochromic devices, electrochemical devices etc, microwave technology extract the microwave absorbing ability of electrically conducting polymers. The conducting polymers are widely used in its potential applications like electro magnetic interference shielding, satellite communication links, beam steering radars, frequency selective surfaces etc. Considering the relevance of microwave applications of conducting polymers, the study of microwave properties of conducting polymers stands poised to become a compelling choice for synthetic chemists and condensed - matter physicists, physical chemists and material scientists, electrochemists and polymer scientists.

The main aim of the present work is to study the microwave and low frequency properties of various conducting polymers, conducting semi-interpenetrating networks, conducting copolymers and to characterise it. Also this thesis collated the microwave properties of these conducting systems and exposes the various technologically important applications in the industrial, scientific, communication and defence applications.

Content of the thesis

The thesis consists of seven chapters

- **Chapter 1** presents a review of the literature in this field and the scope of the present investigation.
- **Chapter 2** deals with the materials used and the experimental procedures adopted for the study.
- **Chapter 3** is divided in to three parts; Part I reports the dielectric properties of polyaniline alone in powder and pellet forms in the microwave field. The effect of preparation temperature, different dopants, concentrations of dopants and drying conditions on the dielectric properties of polyaniline was studied. The characterization using IR spectroscopy was also included in this part. Part II reports the synthesis and the dielectric properties of polyaniline - polyvinyl chloride semi interpenetrating networks (Pani: PVC SIPN) in powder, pellet and film forms. Different compositions of Pani: PVC SIPN's were prepared and the dielectric properties were evaluated. It also includes the thermal stability studies, conductivity in the low frequencies, and scanning electron microscopy (SEM) analysis. A detailed comparison of the dielectric properties of Pani alone, Pani: PVC SIPN in various forms was included. The thermal stability and the Tg of powder and film form were also compared in this section. The dielectric properties of film form (solvent soluble) are much higher than the powder and pellet forms. Part III comprises the studies on the dielectric properties of Pani: natural rubber (Pani:NR)composite and SIPN. The natural rubber was compounded with polyaniline and its dielectric properties in the microwave field and the thermal stability were studied. Pani :NR SIPN was also prepared using in-situ polymerisation technique and it was characterised by IR, TGA and DSC. The probability of core- shell structure of this SIPN was also revealed in this section.
- **Chapter 4** is divided into two parts. Studies on poly o-toluidine alone and its copolymer with polyaniline in the microwave field constitute part I. A detailed characterisation of the copolymer using IR spectroscopy, TGA, DSC were also included in this part. The dielectric properties of PoT alone and the copolymer

were compared. Improvement in the dielectric properties was observed in copolymer. Part II deals with the synthesis, characterisation using TGA and SEM of poly o-toluidine- polyvinyl chloride SIPN (PoT:PVC SIPN) in pellet form and solvent soluble (film) form of various compositions and their dielectric properties in the microwave field.

- **Chapter** 5 is divided into two parts. Part I deals with the studies on poly pyrrole alone and poly pyrrole-polyvinyl chloride semi interpenetrating networks (PPy: PVC SIPN) using ferric chloride as the initiator. Different compositions of PPy: PVC SIPN was prepared and the dielectric properties in the microwave field was studied. The thermal stability of PPy alone and the SIPN's were also evaluated. Part II deals with the synthesis of poly pyrrole and its SIPN's with PVC (in pellet and film forms) using ammonium persulphate as the initiator and the characterisation of polypyrrole using IR spectroscopy. The detailed evaluation of the dielectric properties of PPy alone, PPy:PVC SIPN of different compositions in the microwave field was reported. Also the conductivity of PPy alone and the SIPN in the low frequency was also studied. A detailed comparison of the dielectric properties of polypyrrole prepared by two initiators, their thermal stability etc were reported. Also a comparison of dielectric properties, thermal stability and Tg of pellet and film form of SIPN was included.
- **Chapter** 6 was divided in to three. Pat I deals with the comparison of dielectric properties in the microwave field of all polymer matrices that was used in the study. Part II deals with the important applications of this investigation and part III comprises the future out look of the present investigation.
- **Chapter** 7 comprises the summary and conclusions derived from these studies.

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

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Chapter 1

INTRODUCTION

While polymers are generally well known for their electrical insulation characteristics a few of them are potential candidates for a number of applications that require good electronic and/or ionic conductivity. Outstanding properties in one area alone, for example, conductivity, is not necessarily a guarantee of practical utility as several factors such as cost, processability, mechanical integrity, and the quality of polymer - electrode contact come into consideration. Some of these issues are addressable with organic polymers due to its ability to fine - tune properties through backbone and/or chain functionalization. Indeed, the current resurgence in interest in electropositive polymers stems from the clever application of synthetic chemistry to the design of useful materials.

1.1 HISTORY

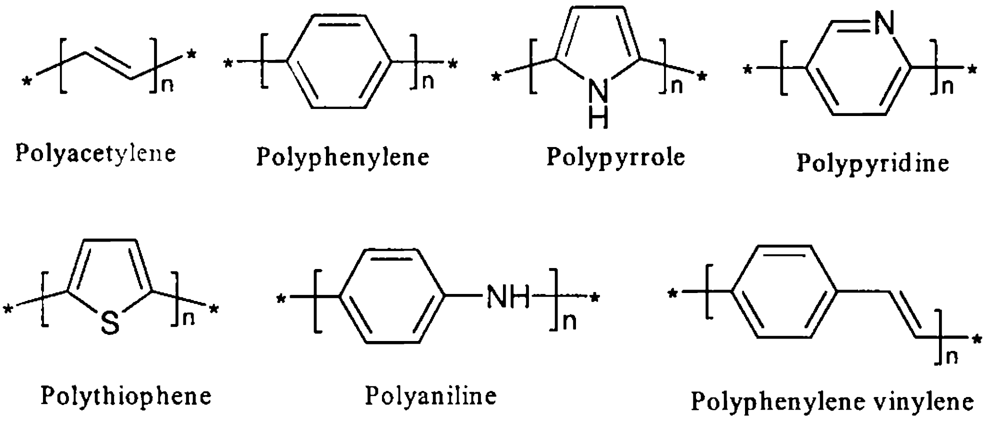
Until about 30 years ago all carbon-based polymers had been extensively used by the electronics industry as insulators. These materials are commonly used for insulating copper wires and as outer structure of electrical appliances, which prevent people from direct contact with electricity. But during the beginning of 1960's the research priorities at the Plastics Research Laboratory of BASF in Ludwigshafen, Germany centered on postulating new structural properties of polymers made by oxidative coupling. Copper chloride and aluminium chloride were used to make an oligobenzene from benzene. This reaction was extended to include other aromatic and heterocyclic compounds. The products were characterized in terms of thermo electrical power, photo and dark electrical conductivities. To their surprise, polyphenylene and polythiophene showed electrical conductivities up to .1 S/cm. Not only was this highest value yet obtained, but also it was the first matrix capable of conducting electricity.

Highly sophisticated industry such as microelectronics has demanded greater attention for research and development for newer materials having good physical and electrical properties. The thirst is primarily in the direction of generating those organic conducting materials, which could replace and eventually avoid the large -scale commercial exploitation of the earth's natural reserves such as copper, bronze and iron. A number of organic semiconductors such as phthalocyanines[1, 2] microcyanine[3, 4], $(SN)_x$[5], chlorophyll[6] have been developed of which some have found uses in solid state devices such as solar cells[7] and schottky junction[8].

A significant breakthrough occurred in 1977 with the discovery of polyacetylene by Shirakawa et al[9]. Polyacetylene containing conjugated single and double bonds in its structure becomes electrically conductive after carrying out a structural modification called "doping". Since the discovery of polyacetylene, research efforts were focused on synthesis and characterization of novel polymers with π conjugated backbone due to their interesting optical, electrochemical and conducting properties.

1.2 π CONJUGATED POLYMERS

During the last two decades, research in π conjugated polymers have witnessed an increase in interest from academic and industrial research laboratories aiming at design and synthesis of new materials in combination with the characterization and application of their novel functional properties[10,11]. These efforts have resulted in a large family of π conjugated polymers known today (figure1.1)[12] which exhibits a series of attractive properties such as tunable electrical conductivity[13], photoconductivity[14], charge storage capacity[15], photoluminescence[16], and electroluminescence[17].



Polyacetylene Polyphenylene Polypyrrole Polypyridine

Polythiophene Polyaniline Polyphenylene vinylene

Figure 1.1: Structures of selected π conjugated polymers.

Conjugated polymers are organic semiconductors that hardly differ from inorganic semiconductors in their electronic levels. Both have their electrons organized in bands rather than in discrete levels and their ground state energy bands either completely filled or completely empty[10,11]. The band structure of a conjugated polymer originates from the interaction of the π orbitals of the repeating units throughout the chain. This is exemplified in figure 1.2; where the calculated (frontier) energy levels of oligothiophenes with n = 1 - 4 and of polythiophene are shown as a function of oligomer length[18].

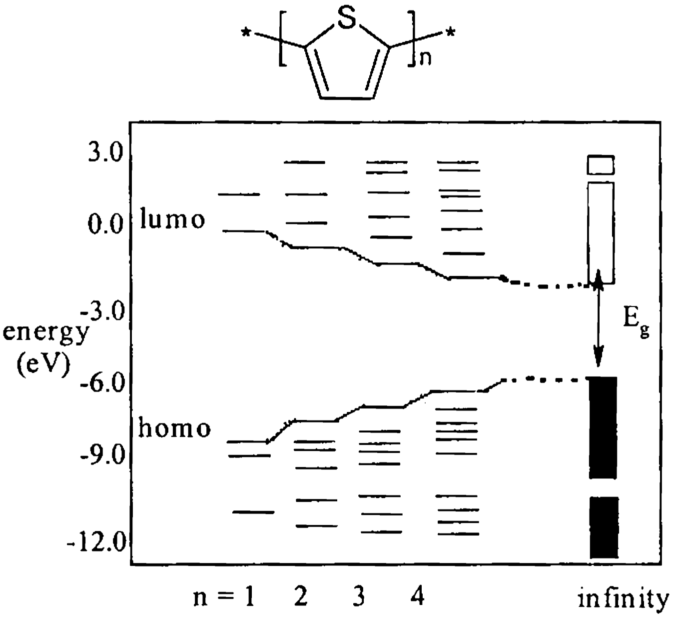


Figure 1.2: Frontier energy levels of oligothiophenes with n = 1 - 4.

Defect free conjugated polymers can be considered as a one-dimensional system with one electron per carbon atom. The typical energy gap between the conduction and the valance band is 1 to 3 eV. Since it is highly unlikely that excitation of carriers would occur across a gap of 2 eV, these systems would be insulators or at best semiconductors. The π conjugated polymer is transformed into a conductor by doping it with either an electron donor or an electron acceptor. Introduction of dopants give rise to strong electron - phonon interactions, leading to new quasi particles, solitons[19,20], bipolarons,[21-22] and polarons[23].

1.2.1 *Charge carriers: polarons, bipolarons and solitons*

Charge carriers in conjugated polymers can be generated through chemical or electrochemical doping. The basic structural motif of conjugated polymer is an alternating sequence of single and double bonds. The prototype conjugated polymers (trans polyacetylene) has a degenerate ground state in which there is no preferred sense of bond alternation.

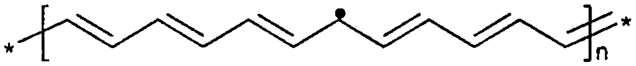


Fig.1.3: Soliton in polyacetylene.

Most conjugated polymers, however possess a non-degenerate ground state with a preferred sense of bond alternation. Oxidation of trans polyacetylene generates a cation radical. As there is no preferred sense of bond alternation, the positive charge and the unpaired electron of the cation radical can move independently along the polymer chain, forming domain walls between the two identical parts of bond alternation. In solid state physics, a charge associated with a boundary or domain wall is called a 'soliton' (figure 1.3) in the language of field theory[24-27]. It has the properties of a solitary wave. That is, it can move without deformation and dissipiation[28]. The unpaired electron can be considered as a neutral soliton or an excitation of the system that separates two potential wells of the same energy. Charged solitons (anions or cations) can explain the spinless transport since they carry charge but no spin.

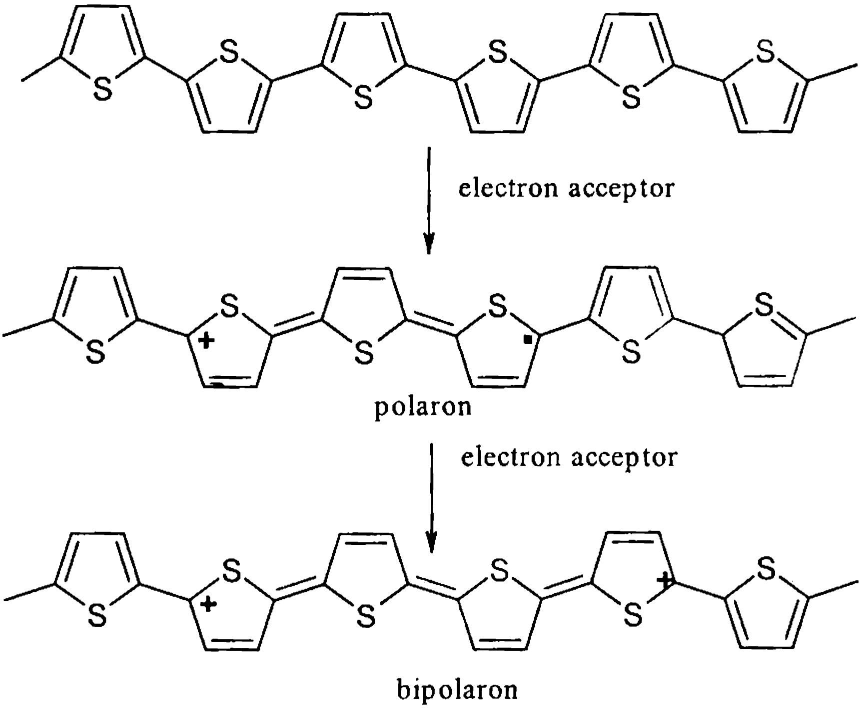


Figure 1.4: Polaron and bipolaron.

Oxidation or reduction of nondegenerate ground state polymers such as polythiophene or polypyrrole have a different result. The initially formed cation radical possess both spin and charge[29] and cannot move independently. A 'polaron' is either a positively charged hole site (radical cation) or a negatively charged electron site (radical anion). It has a lattice relaxation (distortion) around the charge. Theoretical models[21] demonstrate that two radical ions (polarons) on the same chain-react exothermically to produce a dication or dianion called a 'bipolaron', which accounts for spinless conductivity in these polymers. A typical polaron and a bipolaron are shown in figure 1.4.

1.2.2. *Applications of conjugated polymers*

- **Light emitting diodes.**

Although not used for device fabrication, electroluminescence (EL) from organic semiconductors has been known for a considerable time[30]. Since Tong et al[31] have reported efficient electroluminescence from organic hetero junction using tris(8-hydroxy)-quinoline aluminium, research in organic light emitting diodes have attracted considerable interest from display applications.

Burroughes et al[17] first demonstrated that polyphenylene vinylene (PPV) can be used in electroluminescent device fabrication. The typical quantum efficiency of PPV based device was reported to be .01%. In contrast EL devices using ITO (Indium-Tin-Oxide) coated glass and aluminium as electrodes, fabricated from Son's[32] PPV has an efficiency of 0.22%. Insertion of an electron transport layer such as 2-(4-biphenyl)-5-(4-t-butyl phenyl)-1,3,4- oxadiazole (PBD)[33] between the light emitting layer and the electron-injecting electrode increases the device efficiency by a factor of 5 to 10. A bilayer EL device with a poly (cyanophthalylidene) (PCP) layer inserted between PPV and the electron injecting electrode exhibits a red emission from 'PCP'[34] with a quantum efficiency of 4%. Yang and Heeger[35] have reported an improved EL device efficiency when the ITO glass hole-injecting electrode is replaced with polyaniline. Conjugated polymers that emit in the red [poly (2-methoxy 5-(2'-

ethoxy-p-phenylene vinylene)][36], and poly (cyanophthalylidene)[37], yellow green (PPV)[17], blue [poly (p-pyridine)][37], violet blue [poly(N-vinyl carbazole)][38], yellow orange [poly(p-pyridyl vinylene)][39], orange-red [poly(3-alkyl thiophenes)][40], and green [poly(3-cyclo hexythiophene)][41] wavelengths have been reported.

- **Lithography**

Angelopoulos etal[42] and Huang[43] demonstrated that electrically conducting conjugated polymers [polyacetylene][42] or [poly (3-alkyl thiophene)][43] used as a sandwich layer between the silicon wafer and the resist eliminates the charging problem of the resist substrate in lithography. When an interlayer conductor is not present a pattern displacement with respect to a reference pattern of as much as 5 μm is observed. With the incorporation of a conducting polyacetylene inter layer, zero pattern displacements are observed.

- **Sensors**

The electronic conductivity of the conjugated polymers decrease by a factor of 10^5 or more upon introducing defects and rotations around single bonds that imparts non-planarity to the polymer backbone[44]. Swager and coworkers[45] have recently shown that this large dynamic range can be exploited for sensor applications.

- **Energy storage applications**

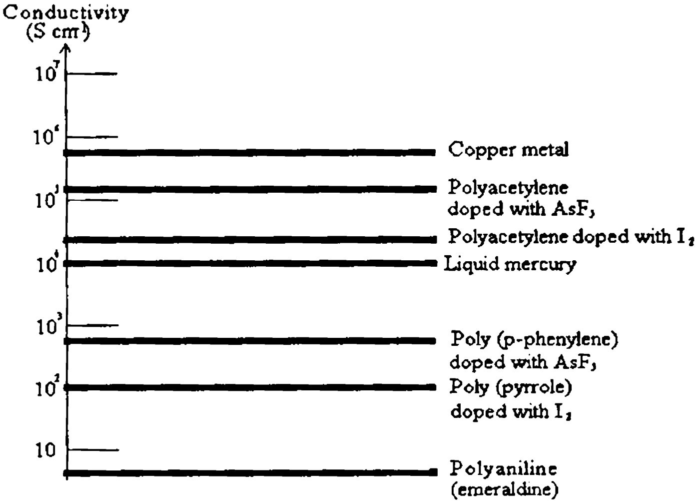
Organic conjugated polymers have several advantages over inorganic electroactive materials such as higher operating cell voltages, higher energy density, longer lifetime, potentially less toxic and ease of molding to the desired shape. Other factors are lower cost, rechargeability and cycleability.

Besides the attractive material properties and applications, the power of conjugated polymers is to be found in the case of manipulation with their chemical structure. Since π conjugated polymers allow virtually endless manipulation of their chemical structure, control of band gap of these semiconductors is a research issue of ongoing interest. This 'band gap engineering' may give the polymer its desired electrical and optical properties and reduction of the band gap to approximately zero is expected in materializing an intrinsically conducting polymer[46,47].

1.3 ELECTRICALLY CONDUCTING POLYMERS

Since a conjugated polymer is a semiconductor with a finite band gap, conversion into a conductor implies introduction of charge on to these polymer chains by various methods like oxidation or reduction, acid doping etc.

A major breakthrough in the search for conducting polymers occurred in 1977, with the discovery that polyacetylene[9,48,49] could be readily oxidized by electron acceptors such as iodine or arsenic pentafluoride or reduced by donors such as lithium. The resulting material had conductivity of magnitude several orders greater than the original untreated sample. The redox reaction can be carried out in vapour phase, in solution or electrochemically. A significant development occurred in 1979 with the discovery that poly (p-phenylene)[50] could also be doped to high conductivity. In the preceding years, polyheterocyclics and polyaromatics especially polypyrrole[51,52], polythiophene[53-55], polyfuran[56], polyindole[57], polycarbazole[58], polypyrene[59], polyaniline[60] etc, have commanded greater importance and increased respectability among the entire field of conducting polymers not only because of their high electrical conductivity by doping and relative ease of preparation but also because of the potential technological applications. The relative conductivities of some of the polymers are shown in figure 1.5.



Logarithmic conductivity ladder locating some metals and conducting polymers

Figure 1.5: Logarithmic conductivity ladder.

1.3.1. Conduction mechanisms

1. Band theory

One early explanation of conduction phenomena in conducting polymers used band theory[44,61]. According to this model when two atoms having half filled orbitals are brought close enough to each other for the orbitals to overlap, their interaction results in the formation of two molecular orbitals. The energy difference (E_g) between the newly formed orbitals is determined by the degree of overlap between the conducting orbitals. As the degree of overlap is different for every pair of orbitals, a low energy band (valence band) 'VB' and a high-energy band (conduction band)'CB' are formed.

The extent of occupation of energy bands and the energy gap between them determine the conductivity of a material. Either the partially filled 'VB' or an overlap between the 'VB' and 'CB' characterizes metals. This implies a complete freedom of movement for the charge carriers under the influence of an applied field.

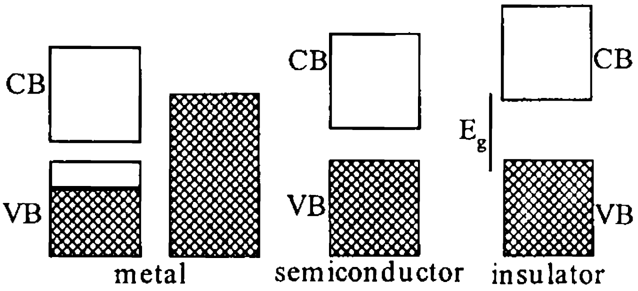


Figure 1.6: Band model of conductor, semiconductor and insulator.

In semiconductors and insulators 'VB' is completely filled and the 'CB' is empty. Therefore conduction can only take place when charge carriers are promoted from the 'VB' to the 'CB'. In semiconductors the excitation of charge carriers is possible.

The basic concepts of band model are also applicable to conducting polymers. The conjugation length is an important parameter influencing the conductivity[62-64].The carrier mobility and consequently the conductivity increase with increasing conjugation length. Because conjugated polymers do not extend over the full specimen, charge carriers have to move along the extended л system of the conjugated backbone (intrachain conductivity) as well as between the individual molecules (inter chain conductivity)[65].

Several models have been proposed for the intra and inter chain conductivity but all proposed models have not been fully validated.

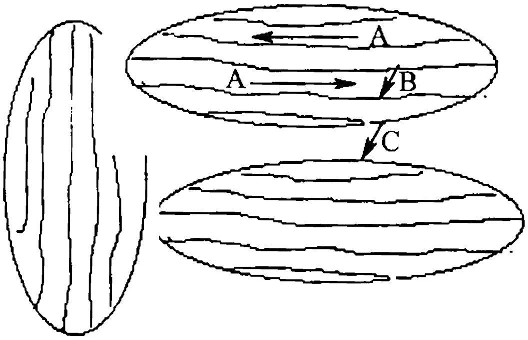


Figure 1.7: Conductivity network of a conducting polymer

(A- intra chain transport, B- inter chain transport, C- inter particle transport).

In conducting polymers like trans polyacetylene two energetically equivalent resonance structures are possible. At the conversion points of these structures unpaired electrons are present called solitons. This conversion point is actually spread out over several (2-10) bonds[63, 64].

Solitons introduce a localized electronic state in the middle of the energy gap between 'VB' and 'CB' of polyacetylene (figure 1.8).

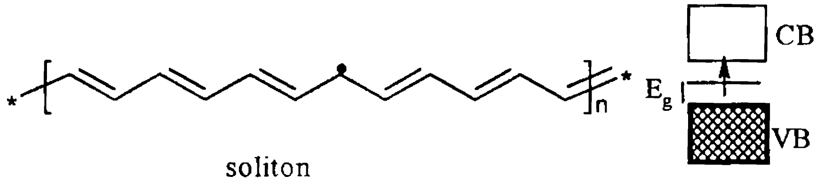


Figure1.8: Localised energy state of polyacetylene on doping

Other conjugated polymers like polythiophene, polypyrrole, do not have a degenerate ground state, but different resonance structures can be present and therefore unpaired electrons are formed at the conversion points. These electrons polarize the local environment, which then relaxes in to a new equilibrium position. This induces two electronic states in the band gap facilitating conductivity. The combination of charge carrier and its distorted environment is called a polaron (figure 1.9). The chemical equivalent is a charged radical[66].

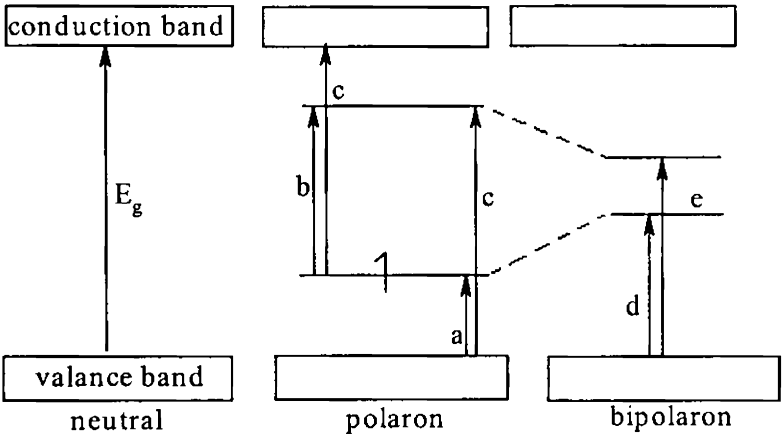


Figure 1.9: The electronic transitions for various redox states indicated by the arrows (e.g., a-e)

2. Doping

Conjugated polymers in their undoped state are either insulators or semi conductors. In the case of polyacetylene the conductivity is 10^{-9} S/cm for cis and 10^{-5} for trans form. Also poly p-phenylenes in the absence of dopant are insulators with a conductivity of 10^{-12} S/cm. In the undoped conditions the charge carrier concentration is low since the band gap is high. Eventhough the conjugated structures are very much suitable for conduction due to high carrier mobility, the low carrier concentration reduces the conductivity. Conductivity 'σ ' is proportional to the number of charge carriers (n) and the carrier mobility (μ).

I.e., $\sigma = e\, n\, \mu$, where 'e' denotes one electron charge.

The charge carriers can be generated by oxidation or reduction of the polymer and the process is called doping. Upon doping of polymers, charge is transferred from the dopant to the polymer[44]. Oxidation of polymer (electron from polymer to dopant) results in a hole-conducting polymer (p-type) whereas on reduction electron-conducting polymer (n-type) is formed[11]. In order to maintain charge neutrality counter ions are also incorporated. Counter ion lower the mobility of the charge carriers due to their interaction with the charge carriers on the conjugated polymer called pinning effect[67]. This pinning effect is less when the size and the degree of charge delocalization on the counter ion is larger.

Further more, stability of the conductivity shows a positive relation with the size of the counter ion[68] whereas the diffusion rate of the counter ion into the doped layer shows a negative relation with the size[69]. Doping of polyacetylene results in the formation of new, neutral solitons and the charging of both newly formed and already existing solitons. The chemical equivalents are carbocation or anion (polarons) and carbodianion or dication (bipolarons). Doping of conducting polymers other than polyacetylene results in the formation of polarons and further oxidation/reduction of newly formed and already existing polarons. The increase in conductivity upon doping can be as high as 14 orders of magnitude for different dopant combinations[70,71]. Upon n-type doping organic anions that are highly unstable towards air and water are formed. Consequently, the conductivity generated by n-type doping is less stable than by p-type doping. Therefore p-type dopants are more frequently used. The p-type dopants include strong and weak agents such as ASF_5[72] and I_2[72], Br_2[73], IF_5[74], SbF_5[75], $AlCl_3$[76], O_2[77], NO_2PF_6[78], $FeCl_3$[79, 80]. Some typical n-type dopants are sodium naphthalide in tetrahydro furan[81], potassium naphthalide[82], molten potassium or sodium. Electrical conductivities of conjugated polymers with selected dopants is shown below.

Polymer	Dopants	Conductivity (S/cm)
Polyacetylene	I_3^-	550 [83]
	AsF_6^-	1100[83]
	BF_4^-	100 [83]
	K^+	50 [84]
Poly (p-phenylene)	I_3^-	< 10-5[85]
	AsF_6^-	500[85]
	K^+	20[85]
Polypyrrole	I_3^-	600 [87]
	AsF_6^-	100[87]
	BF_4^-	100[87]
	K^+	<10-5[86,87]
Polythiophene	I_3^-	.1 [88]
	AsF_6^-	10 [88]
	BF_4^-	100[89]

Since optical properties and oxidation /reduction potentials of mobile charge carriers vary for short chains and eventually become invariant for longer ones, it is desirable to have control over the molecular weight of the conducting polymer. This control can be achieved by choosing an appropriate polymerization method.

1.3.2 Synthesis of conducting polymers

Since the conductivity of conducting polymers are known to depend on the method of synthesis, a large number of preparatory methods have been developed. Conducting polymers are synthesized by using a number of polymerization methods such as chain growth (addition), step growth (condensation), electrochemical, ring opening and plasma polymerization.

- **Chain growth polymerization.**

Many conducting polymers are synthesized by chain growth. The process includes initiation, propagation and termination steps. A typical example is the synthesis of polyacetylene.

Shirakawa and co-workers were able to obtain polyacetylene in a film form using soluble ziegler-natta catalyst[90]. In Shirakawa's method acetylene gas is blown to a solution of the catalyst [Ti (OCH$_4$: Al (C$_2$H$_5$)$_3$, 1:4] in toluene (figure 1.10).

$$n\ CH \equiv CH \xrightarrow[20\ min.]{-78\ ^{0}C,\ catalyst} -\!\!\left(CH = CH\right)\!\!-_{n}$$

Fig. 1.10: Polymerization of acetylene.

The thickness of resulting film is controlled by the reaction time. A coating with a metallic sheen appears immediately on the wetted surface, it is easily removed to provide a freestanding polyacetylene film. A variant method developed by Naarmann and Theophilon [91] uses aged butyl lithium in silicon oil, as catalyst and the polymerization was done at room temperature. Produced as above, polyacetylene exists predominantly as the cis isomer with a high degree of crystallinity. Isomerization to the more stable trans form can be induced by heat (figure 1.11) or dopants[92-96].

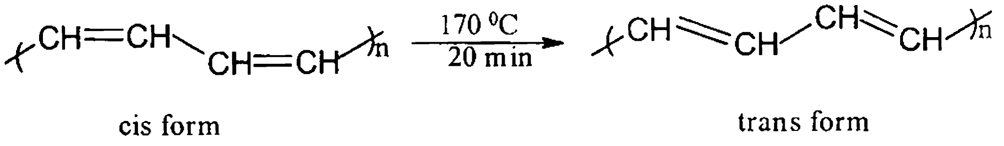


Fig.1.11: Isomerization of cis form of polyacetylene to trans form.

➢ *Step growth polymerization*

In step growth polymerization small molecules are eliminated from the monomers in the process of forming the polymeric material. The molecular weights of polymers prepared in this manner depend on the conversion and high polymers are obtained only in conversion of the order of 99% or higher. Typical examples for step growth polymerization are given below.

(a) Poly (P-Phenylene)[PPP]

One of the most effective technique consists of using a benzene-aluminium chloride cupric chloride system[97, 98]. A quantitative yield is obtained with a molar ratio of $AlCl_3$: $CuCl_2$ (2:1)(figure 1.12).

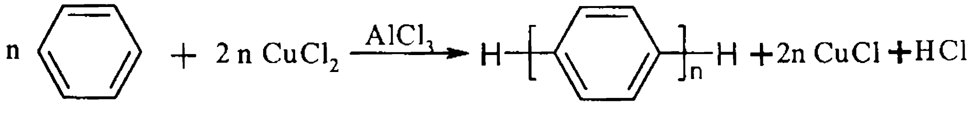


Fig. 1.12: Synthesis of Poly (P-Phenylene).

Poly P-Phenylene was also synthesized by the reactions of haloaromatic called Ullman reaction, in which copper [99] is used as the catalyst.

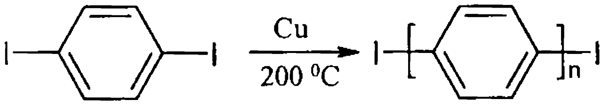


Fig.1.13: Ullman reaction

(b) Poly p-phenylene sulfide[PPS)

One of the most thoroughly studied and used reactions, macallum reaction, involves treating halobenzenes with sulfur and sodium carbonate in a sealed container at 275-360°C[100,101] (figure 1.14). Another method was simple coupling reaction (figure 1.15).

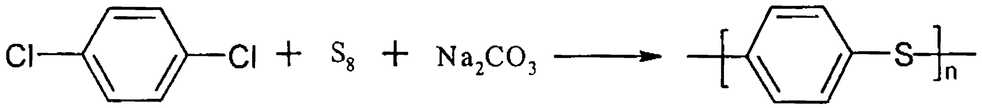


Fig.1.14a: Macallum reaction

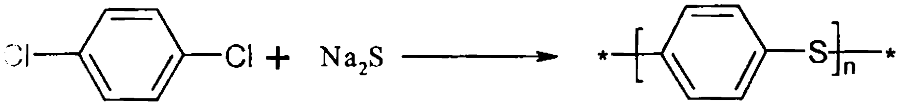


Fig.1.14b: Coupling reaction

(c) Polythiophene

Most commonly used method is the grignard coupling of dihalothiophenes with transition metal complexes [102].

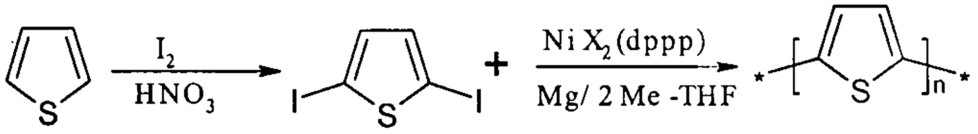


Fig.1.15: Preparation of polythiophene through grignard coupling.

(d) Poly aniline

Powder form of polyaniline is synthesized chemically[103] by the oxidative polymerization of aniline in an aqueous acidic medium with an inorganic oxidant. Preferred method is to use HCl or H_2SO_4 with ammonium persulfate as an oxidant. Depending on the number of protons and electrons in the polymer backbone, poly aniline can have a number of different forms and a wide range of oxidation states (figure 1.16a, 1.16b and 1.16c).

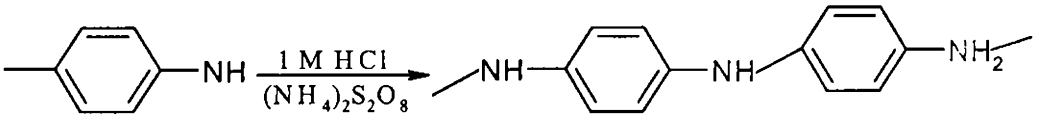


Fig.1.16 a:leuco emeraldine

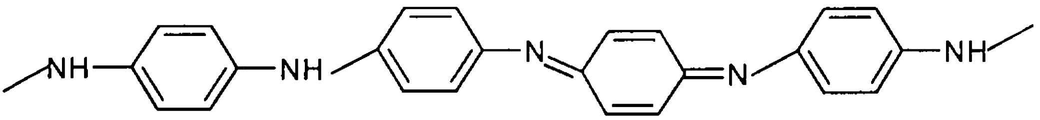


Fig.1.16 b:emeraldine base

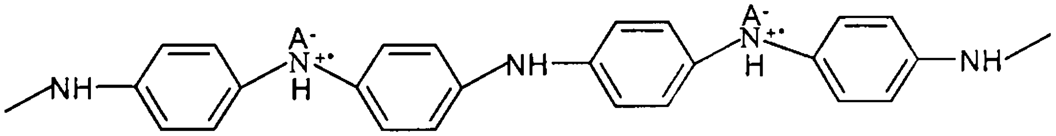


Fig 1.16 c:conducting emeraldine salt

(e) Poly (P-Phenylene Vinylene) [PPV].

Burroughes and co-workers[104] reported a synthetic procedure for the synthesis of PPV from a soluble prepolymer. The tetrahydro thiophene group is readily displaced by a hydroxy group[105,] which is then oxidized to a carbonyl group[106], crystalline trans form of PPV was formed. The synthesis is explained in figure 1.17.

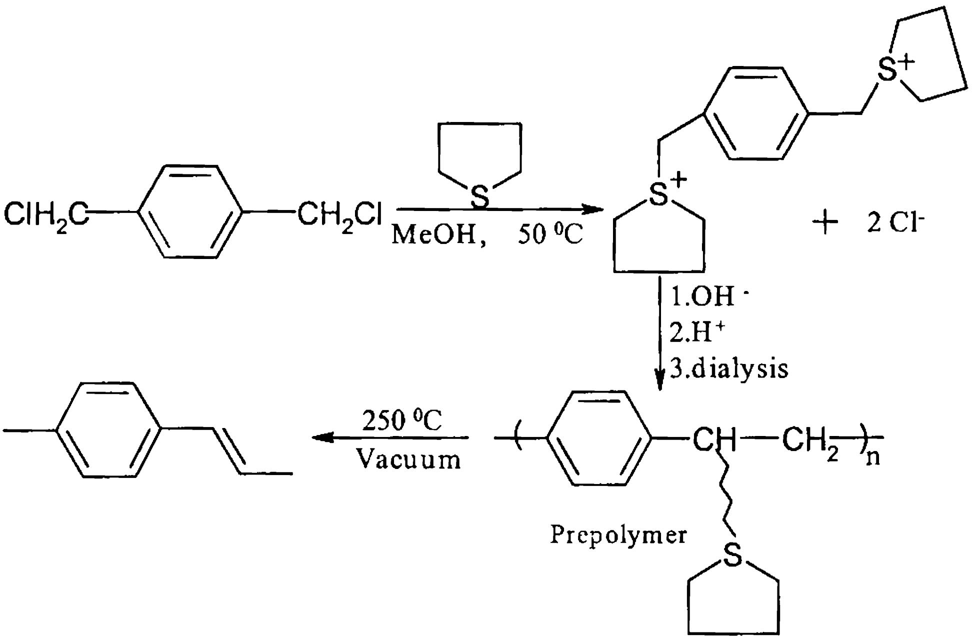


Fig.1.17: Synthetic route and polymer structure of poly p-phenylene vinylene.

> ***Electro chemical polymerization.***

Most of the conjugated polymers like poly pyrrole, poly thiophene, poly aniline, poly p-phenylene can be synthesized by electro chemical process[107]. In electrochemical polymerization, the monomer and electrolyte are dissolved in a suitable solvent and is polymerized at low voltage. The polymer growth is on the surface of the anode. Both reductive and oxidative polymerization is possible, but the oxidative method is more commonly used.

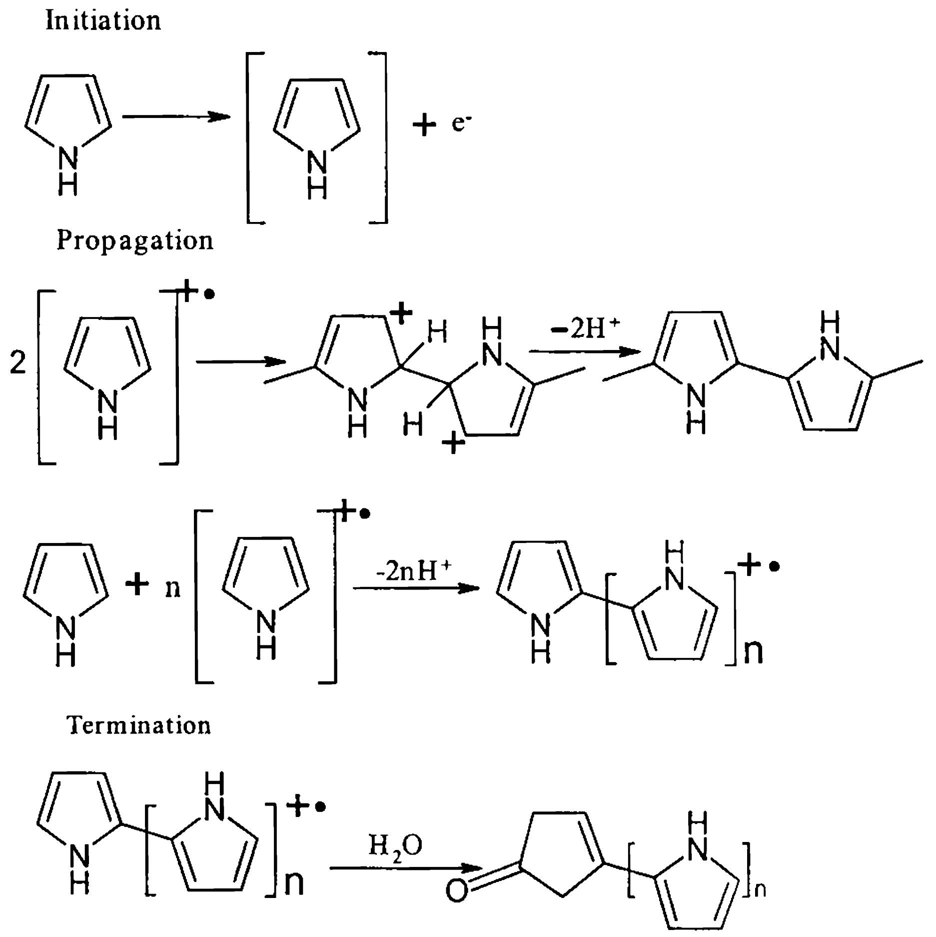


Fig.1.18: Electro polymerization of pyrrole.

The electrochemical polymerization of polymers starts with the one electron oxidation of monomers and it will generate a radical cation. This radical cation then forms a dimer and as the reactivity of dimer is high it will propagate.

During the dimerisation, 2 C-H bonds are converted to 2 C - C bonds along with 2 H^+.

- ***Metathesis polymerization(Ring opening metathesis polymer (ROMP)***

In metathesis polymerization one of transition metal carbene complex is used to cut open olefin molecule and stitch the molecules back together into a polymer chain[108]. This method is of great significance for the synthesis of conjugated polymers because the number of double bonds in the monomer is preserved in the polymer. And in principle one can take the repeat unit for any conjugated polymer containing an olefin and cyclise it to form a potential new monomer. Usually the monomer used is a circle of double bonds i.e., cyclic octa tetrene (COT). This monomer is synthesized by the tetramerization of acetylene with catalyst. The schematic representation is given in the figure 1.19.

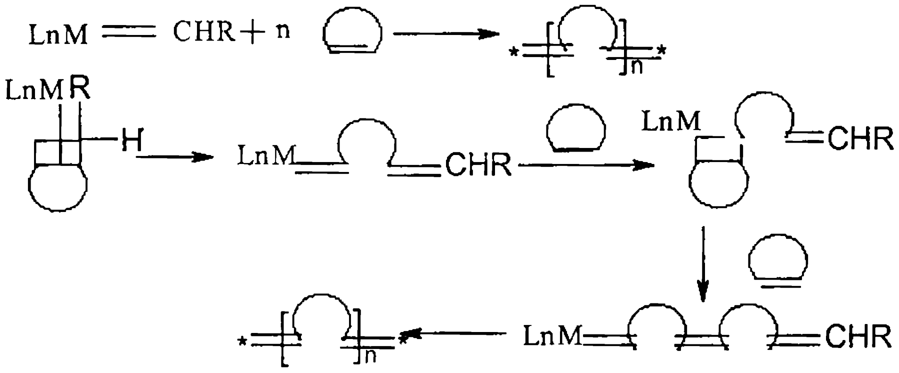


Fig.1.19: Scheme for ring opening metathesis polymerization of polyacetylene.

1.4 ADVANTAGES AND DISADVANTAGES OF CONDUCTING POLYMERS

Advantages	Disadvantages
♦ High electrical conductivity. ♦ Conductivity can be controlled by varying the dopant concentration. ♦ Good mechanical properties. ♦ Ease of bulk preparation. ♦ High environmental stability. ♦ High temperature resistance. ♦ Low cost. ♦ High anticorrosion property.	♦ Very difficult to process. ♦ Stability of dopant is poor

The processability and stability of important conducting polymers are shown in table 1.1.

Table 1.1

Polymer	Processability	Stability(doped state)
Polyacetylene	Limited	Poor
Polyphenylene	Limited	Poor
Poly(p-phenylene vinylene)	Limited	Poor
Polypyrrole	Good	Good
Polythiophene	Good	Good
Polyaniline	Good	Good

1.5 METHODS TO ENHANCE THE PROCESSABILITY OF CONDUCTING POLYMERS

Without processability, the appreciation for conducting polymer would be limited one. Many approaches to making tractable materials have been explored, including

- The preparation of blends, composites and interpenetrated network.
- The synthesis of random, graft and block copolymers.
- Use of precursor polymers.

Conducting polymer composites have drawn considerable interest in recent years because of their numerous applications in a variety of areas of electrical and electronic industry [109,110]. Incorporation of conducting polymers into a host polymer substrate, forming a blend, composite or interpenetrated bulk network has been used as an approach to combine electrical conductivities with desirable mechanical strength of polymers[111]. Interpenetrating network conducting polymer result through in-situ polymerization of monomers of conducing polymers inside the matrices of conventional linear polymers.

Conducting polymer blends with unusually low percolation threshold has been reported for polyaniline and styrene - butyl acrylate copolymer blends[112]. Polyaniline epoxy novolac resin composite has been reported to be useful for antistatic applications[113]. Interpenetrating networks of polypyrrole filaments is swellable insulating plastic matrices have been produced in electro chemical cells[114,115]

Inorder to improve the solubility of conducting polymers, copolymers are prepared. Copolymer of acetylene and methyl acetylene[116], a soluble polyene, was more tractable than poly acetylene itself. When the polyene block is short, dark purple solution of the co polymer in common organic solvents are obtained. Co-polymers of acetylene and phenyl acetylene containing 26% acetylene were soluble in methylene chloride[117]. The solutions are actually micellar aggregates of copolymers[118]. The polyacetylene portion was arranged as an elongated amorphous core.

The discovery of soluble polymers from prepolymers was an important break through in conducting polymer research. An important break through was the discovery of soluble polymers from pre polymers. One of the examples is the preparation of soluble polyacetylene through Durham route[119, 120]. It involves the metathesis polymerisation to give a soluble but thermally unstable polymer. Polymers, slowly at room temperature or more rapidly at 80⁰C, undergoes a vetro-dielo-alder reaction. This reaction results in the formation of amorphous polyacetylene.

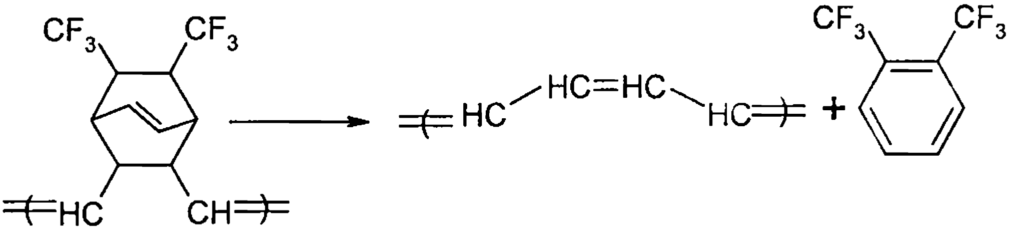


Fig.1.20: Preparation of polyacetylene through Durham route.

1.6 RECENT TRENDS IN CONDUCTING POLYMERS.

The conducting polymers have been extensively studied in recent years because of their significant importance in applied as well as basic sciences. The good mechanical properties and intriguing electronic properties of these materials indicate that they can be used in many device applications. The synthesis processes, various physical properties and potential technological applications of these novel systems have been widely discussed in recent publications. The effect of functional polyelectrolytes in inherently conducting polymers such as PPy has been investigated using cyclic voltammetry[121]. It was found that the 2-acrylanido -2 - methyl - 1 propane sulfuric acid (AMPS) content in poly electrolyte affects the nature of PPy-PE product. As the AMPS content increases, the electrochemical and electrical properties improved.

The effect of temperature on the conductivity of polypyrrole conducting polymer films prepared by an electrochemical method in an aqueous medium using camphor sulfuric acid as the dopant was also investigated[122]. It was observed that with increase in temperature, the conductivity decreases and the optimum temperature for the conductivity is between 10 and 30°C. The results showed that the film formed at lower temperature has higher conductivity and is stronger than that formed at higher temperature. X-ray studies indicate that the interlayer distance increase with increasing temperature. Nano composites of polypyrrole and iron oxide were prepared using simultaneous gelation and polymerization process. The conductivity of the composite shows an increase at 15% of pyrrole concentration. At this concentration a transition from a nonmagnetic to magnetic phase was also observed[123].

Electrically conductive semi - IPN's based on poly aniline and cross-linked polyvinyl acetate was prepared[123]. The conductivity of the SIPN increases with increase in polyaniline content and acidity during the polymerization of polyaniline. The conductivity of the semi-IPN is 0.13 S/cm, with the highest polyaniline content of 19.3 wt.%. An ordered polyaniline nano fibril array film was synthesized with a convenient and feasible method based on the anodic aluminium oxide (AAO) template and its field emission property was investigated[124]. A low threshold electric field of 5-6 V/cm and maximum emission current density of ~5mA/cm^2 are observed, which suggests the material as a new candidate for field emitting applications. Effect of secondary doping of polyaniline (Pani) composites, prepared by in-situ emulsion polymerization of aniline in the presence of chlorosulfonated polyethylene (CSPE) or styrene-butadiene-styrene triblock copolymer and dodecyl benzene sulfuric acid on conductivity were studied[125]. Secondary doping and dedoping process were characterized using UV-VIS spectrophotometry. It was found that the conductivity is increased on removal of secondary doping. The effect of chemical degradation on electrical properties were evaluated on undoped polyaniline[126]. The chemical degradation has been analyzed by several complements, FTIRS, XPS, UV-VIS-IR spectroscopy. In the case of vacuum aging the dominant degradation mechanism consists of breaking of double bonds with simultaneous formation of tertiary amines and crosslinking. In air aged samples, in addition to the above mechanism, oxygen incorporation in a form of ketone-type groups and chain scission occurs. By this degradation, the conductivity decreases due to a decrease in charge carrier mobility.

The nano structures(eg. Nano tubes or nano rods) of polyaniline with an average diameter of 150 - 340 nm and conductivity of 10^{-1} - 10^{0} S/cm, is prepared in the presence of self-assembly acids like HCl, H_2SO_4, H_3PO_4, H_3F_4 as dopants[127]. It was found that the morphology, size and electrical properties of nano structures depend on the dopant structures and the reaction conditions. It was characterized by FTIR, UV-VIS spectrum, XDS and X-ray diffraction. The reliability and practicability of the self assembly method for synthesizing micro tubes or nano tubes of conducting polymers through changing polymer chains[128-130] and dopants[131-133] and using different polymerization methods are also reported. The surfactant function of the dopant seemed to play an important role in the formation of nano structures of conducting polymers[134]. Polymerization of aniline in an organic peroxide system by the inverted emulsion process is reported by D.N. Sathya narayana et al [135]. The synthesis was done using a novel oxidizing agent, benzoyl peroxide, a nonpolar solvent and in the presence of sulfosalicilic acid as dopant and sodium lauryl sulfate as emulsifier. The polyaniline - sulfosalicilic acid salt synthesized shows a conductivity of 2.53 S/cm. The synthesis and characterization of two new soluble poly p-phenylene vinylenes are reported[136]. The polymers are poly (2 - (2′, 5′ - bis (octyloxy) benzene) - 1,4 - phenylene vinylene) (BOP - PPV) and poly (2 - (2′, 5′ - bis (octyloxy) benzene) - 5 - methoxy - 1 - 4 - phenylene vinylene) (BOPM - PPV). The polymers prepared at lower temperatures shows higher electroluminescence. The studies on the effect of crosslinking in polyaniline films shows that the solubility decreases and the strength increases[137]. Morphology and thermal properties of conducting polyaniline/poly amide composite films is also reported[138]. The conducting complex (Pani - CSA) and a matrix, polyamide - 66, polyamide - 11 or polyamide - 10 were dissolved in a mixed solvent and the blend solution was casted on a glass and dried for the preparation of Pani/Polyamide composite film. The conductivity ranged from 10^{-7} to 10^{0} S/cm as Pani-CSA content increases.

The d.c and a.c conductivity of polyaniline polyvinyl-alcohol blends was reported by P.Dutta et al[139]. The frequency range of 1 KH_2 - 5 MHz was adopted. A conductive rubber based composite on EPDM and polyaniline was reported[140]. Pani-DBSA (dodecyl benzene sulfuric acid) acts simultaneously as reinforcement and conductive filler for EPDM rubber. The swelling measurements for blends showed that EPDM is partially soluble. Synthesis of copolymers of aniline with o/m - amino benzoic acid by an inverse emulsion pathway was reported[141]. The copolymer is soluble in organic solvents and the solubility increases with amino benzoic acid content. The conductivity is reported to be 2.5 x 10^{-1} S/cm. Copolymers of aniline and amino benzoic acids by electrochemical routes were also reported[142,143].

High ionic conducting polymer with polysaccharide and its applications was reported[144]. Polysaccharides such as cyano ethyl pullulan, cyano ethyl cellulose and acetyl cellulose are examined for use as matrix polymer and an excellent gel - electrolyte which provided a high ionic conductivity up to 2.4 x 10^{-3} S/cm at ambient temperature and good mechanical strength is obtained. A study on the transport properties of polypyrrole - TiO_2 nano composites was also reported[145]. Electrical d.c. and a.c. conductivity of polypyrrole - TiO_2 nano -composites was studied at low temperature (80K) and in the frequency range of 10Hz-5MHz. The material exhibit a.c conductivity above 1 MHz. A blend of polyaniline - polycarbonate was prepared and the d.c conductivity and its mechanical properties were evaluated[146].

A conducting composite of polyaniline and zinc sulfide was prepared and its d. c conductivity and the microwave conductivity at 'X' band were reported[147]. The composite of Pani 60% and ZnS 40% has shown very high values of both real and imaginary parts of dielectric constant in the X band of M.W frequencies. Synthesis and characterization of a new conducting polymer - poly (P-phenylene diazomethane) was reported[148]. The effect of different solvents like DMF, m-cresol, toluene and methanol are studied. An ESR study of conduction mechanism in doped poly (3-methyl hyphened) polymer was reported[149]. Preparation of conducting natural rubber latex by iodine (I_2) doping of vulcanized NR latex[150] and electrical properties of conducting polyaniline - polyimide blends[151], polyaniline – polychloroprene composite [152], polyaniline – polyvinyl chloride blends[153] were strongly studied.

1.7 CONDUCTING POLYMERS IN MICROWAVE TECHNOLOGY

The microwave 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.

Determination of dielectric properties and the use of dielectric heating for polymer synthesis attribute microwaves an important status in polymer chemistry. Polar starting materials and very often products, allow rapid and controllable syntheses, the dielectric properties themselves being an excellent indicator of reaction progress. The ability to control syntheses with high accuracy and with direct heating of the reactants has the advantage of large potential savings in energy. Economic analyses suggest that the costs of curing polymers may be reduced from 4 - 11 MJ/Kg to 0.3 - 0.5 MJ/Kg by switching to the one of microwaves[154]. Epoxy resins have been most widely investigated because of their industrial importance and as their dielectric properties predispose them to effective microwave induced curing[155]. The synthesis of polyamides[156] and polyurethane films[157] suggests that energy transfer is more efficient with the use of pulsed microwaves than by continuous power. This behaviour is characteristic of a relaxation mechanism due to the movement of chain segments in the macromolecular network[157]. The intrinsic dielectric properties of a substance may be enhanced or reduced by the incorporation of a secondary material[158]. The effect of secondary material upon dielectric or related properties in polymers have been extensively studied using copper [159], aluminium [160], carbon black, fibers [161] or other conducting materials. Inherently conducting polymers are excellent microwave absorbers and make ideal materials for effecting welding of plastics[162].

Fifteen years ago, there were only few works in the field of microwave studies on polymers. The potential applications of polymers in the field of EMI shielding[163] and some data on microwave characterization of different kinds of conductive polymers[164] were reported. Nagai and Rendell[165] have extensively studied dielectric and conductivity relaxation in conductive polymers and have applied their model of electric modules to ionic conductors and polyacetylene. Then Epstein[166] gave an excellent survey of all the works made up to 1986 on a.c properties of polyacetylene and on application of hyper frequency properties of metallic polyaniline to microwave welding [167].

Burr[168] carried out an exhaustive review of the dielectric properties of polymers at microwave frequencies in 1985. In this paper, the loss spectra of several polymers were given as a function of frequency or temperature. Debye[169] has established the molecular origin of different relaxation mechanisms at room temperature for dipolar molecular liquids. He has shown that the applied electric field perturbs the orientation distribution function for the dipolar molecules, leading to a static relative permittivity Є' greater than n^2, where 'n' is the optical refractive index and a dispersion for Є' accompanied by a peak in Є''.

When an electric field is applied to a material, a dipole moment is induced depending on the polarisability. This dipole moment arises from a non-homogeneous repartition of the electrical charges in the material. That repartition corresponds to several types of polarization[170] such as electronic, atomic and orientation polarization. The observation of the frequency dependence of complex dielectric constant (Є*= Є'- iЄ'') , shows that at low frequencies the different polarizations contribute to a high permittivity value, beyond that, each kind of polarization will create one resonance or one relaxation process: Є' decrease and a maximum appears for Є''. The main characteristics of relaxation in the case of conducting polymers is to separate an arbitrary way the static conductivity (σ_{dc}) and the conductivity which is appearing only after a given frequency (σ_{ac})[169].

Recently, few papers dealing with the complex dielectric properties of polymers are published. The most important ones[171, 172] present radio electric measurements on polyaniline at one frequency (6.5 GHz). Complex dielectric permittivity of an ion-containing polymer in the microwave region was reported[173]. Complex conductivity of a conducting polymer composite based on polypyrrole and silicon rubber at microwave frequencies were reported[174]. Dielectric and conductivity relaxations in quaternary ammonium polymer was reported by Bozkurt[175]. Wide range of frequencies say, 10^{-2} to 10^{7} Hz was used for the study. Dielectric loss tangent and permittivity of poly tetra fluoroethylene, high-density polyethylene, and cross-linked polystyrene are studied at temperatures ranging from 28 k to 84 K and frequency of 18 GHz[176]. Also dielectric properties of ionomers based on styrene[177]and polyurethane[178] at microwave frequencies were studied.

In order to optimize the use of microwave absorbing conducting polymers, correlation between structural and electrical properties are very essential. The key parameters affecting conduction properties are clearly the interchain distance and the localization length[179]. The interchain distance can be modified by using ring substituted monomers[180]or counter anions with different sizes[181]. The localization length can be altered by controlling the defect rates in polymer or head to head coupling[182]. Further more, the molecular mass has an effect on the microwave properties.

Temperature and pressure also affect microwave properties. There is a strong temperature dependence of σ_{ac}, since lowering the temperature from 220 to 84 K leads to a decrease of σ_{ac} by a factor of (10^3) [182]. The pressure effect on the level of static conductivity has been studied on poly (alkyl-3 thiophene) films[183].

1.8 APPLICATIONS OF CONDUCTING POLYMERS.

1.8.1. Group - I Electroactive applications

- **Polymer rechargeable batteries**

Conducting polymer is used as electrode material for rechargeable batteries[184]. The electrochemical doping process constitutes the basic electrochemistry of battery. The reversibility of electrochemical doping provides a rechargeable battery system.

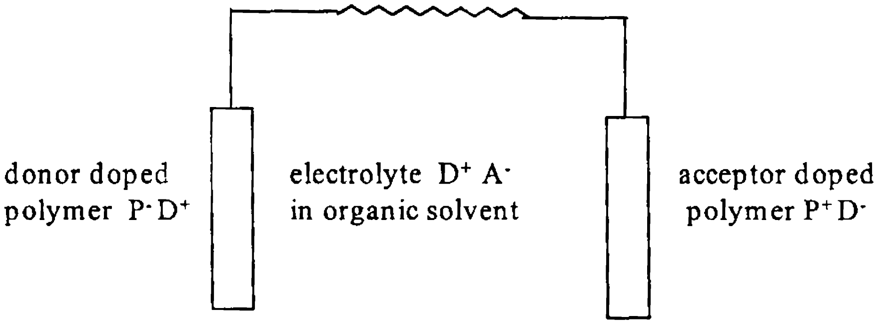


Fig.1.21: Schematic representation of polymer battery (the electrodes are conducting polymers)

- **Molecular electronics**

Molecular electronics deals with the electronic structures assembled atom by atom. An example is a modified polyacetylene with an electron accepting group at one end and a withdrawing group at the other. A short section of the chain is saturated in order to decouple the functional groups. This section is known as spacer or a modulable barrier. There are two inputs, one light pulses excites one end and the other, which excites the modulable barrier. To use this there must be a great deal of redundancy to compensate for switching 'errors'[185].

- **Sensors.**

Biological and chemical sensors based on conducting polymers have several advantages over conventionally used materials[186]. The conducting polymer sensors can be applied in a number of different modes [187], such as pH- based mode, conductometric mode, amperometric mode and potentiometric mode.

Poly pyrrole, poly thiophene and polyaniline are the most commonly used conducting polymers for making sensors.

- **Electrochemical actuators**

The electrochemical actuators utilize the large dimensional charges observed on doping/ dedoping. Here the solid polymer is sandwiched between two polymer electrodes. During the operation of this cell, the dopant can move from one electrode to the other through porous solid polymer electrolyte film, which also acts as a separator. The application of this includes micro tweezers, micro valves and actuators for micro mechanical sorting [188].

- **Electro luminescent devices**

Poly (P-Phenylene Vinylene) and its derivatives have attracted a lot of attention in recent years because of their interesting electro luminescent properties and their potential application as the active emitting layer in light emitting diodes[189]. The device is prepared by sandwiching polymer between the electron-injecting metal (Al or Ca) and a hole injecting metal (Indium-Tin-Oxide).

1.8.2. Group – II Conductivity

- **Antistatic coating applications**

By coating an insulator with a very thin layer of conducting polymer, the build up of static electricity can be prevented. The integrated circuits are more sensitive to static charges and are easily damaged by static discharge at a very low voltage. A conducting polymer can be used to protect it from the electrostatic discharge[190].

- **Conducting adhesives**

By placing monomer between two conductive surfaces and allowing it to polymerise, it is possible to stick these together. This is a conductive adhesive and is used to stick conducting objects together and allow an electric current to pass through them.

- **Printed circuit boards (PCB's)**

The copper-coated epoxy-resins are usually used as PCB's. In order to avoid the drawbacks of expensive plating process, poor adhesion etc conducting plastics are used. This is much cheaper, easy to fabricate and has good adhesion [191].

- **Artificial nerves**

Due to the bio compatibility of some conducting polymers, they may be used to transport small electrical signal through the body, and can act as artificial nerves [192].

1.8.3 Group -III Microwave engineering.

Now a days it is very necessary to study the practical use of microwave properties of conductive polymers because of their wide areas of applications such as coating in reflector antennas, coating in electronic equipment's, frequency selective surfaces, EMI material, satellite communication links, microstrip antennas etc.

The proliferation of electronic devices, those at high frequencies, has brought about new emphasis on shielding of electromagnetic interference (EMI), caused by electric and magnetic fields. To provide shielding, a number of electrically conductive compounds incorporating conductive filler such as copper, silver, nickel and alloys[193-195] have been developed. Later, shielding properties of conductive polymers have been studied as a consequence of their intrinsic conductivity[196,197]. Many works have been done with poly-p-phenylene benzobis-thiazole[198,199] between 2 and 10 GHz. Highly doped polypyrrole films exhibits shielding level above 40 dB in the range 300 MHz to 2 GHz[200,201] while in the case of highly conducting polyaniline these performance vary between 50 and 150 dB for thickness lower than 80 µm[202].

The advancement of microwave technology during world war II has facilitated the use of RADAR for detecting and destroying military aircraft. The military aircraft industry has really taken into account the necessity of reducing the echo (called Radar Cross Section (RCS) of their engines[203]. In order to reduce vulnerability of their aircraft, they looked for a more discrete shape and used materials intended to absorb radar re-emitted energy. The metallic aircraft surface is a reflector from the electromagnetic waves point of view, and therefore for many years much work has been devoted to the conception of radar absorbing materials (RAM) associated with the optimized shape[204]. A significant number of papers deal with the use of conducting polymers in RCS applications. The microwave behaviour of numerous conductive polymers such as polyaniline (1MHz to 2GHz)[205], polypyrrole[206,207],poly-p-phenylene [208], polythiophene[208], poly-p-phenylene vinylene[209] have been published.

1.9 SCOPE AND OBJECTIVES OF THE PRESENT WORK.

The work devoted to investigate the properties and applications of conducting polymers in microwave frequencies is meagre when compared with the volume of literature available on conducting polymers. The primary objective of the investigation has been to explore the dielectric properties of selected conducting polymers in the microwave frequencies and to highlight its technological importance.

The specific objectives of the work are

1. To prepare and study the effect of drying conditions and dopants on the dielectric properties of poly aniline, poly o- toluidine, polypyrrole and to study the influence of the method of preparation on the dielectric properties of poly pyrrole.
2. To prepare and characterize semi interpenetrating polymer networks based on poly (aniline-polyvinyl chloride), poly (aniline-natural rubber), poly (o-toluidine-poly vinyl chloride), and poly (pyrrole-polyvinyl chloride) in various forms and to evaluate their dielectric properties in the microwave frequencies.
3. To study the effect of lower frequencies on the conductivity of polyaniline, poly pyrrole and their selected semi interpenetrating networks.
4. To prepare and characterize poly (o-toluidine-aniline) copolymer and to study the dielectric properties.
5. To compare the important properties of selected conducting polymers and to find the specific areas of applications.

1.10 REFERENCES

1. F.R.F. Fan and L.R. Faulkner, *J. chem. phys.* 69, 3341 (1978).
2. G.C.S. Collins and D.J. Schiffrin, *J.electro-analyt. chem.* 139,335 (1982).
3. G.A. Chamber lain, P.J. Cookney and S.C. Dennisson, *Nature* 284, 45 (1981).
4. A.K. Ghosh and T.Feng, *J.Appl.phys.* 49,5982 (1979).
5. G.B. Street and R.L. green, IBM, *J. Res. Dev.* 34, 577 (1975).
6. C.W. Tang and A.C. Albercht, *Nature* 254, 507 (1975).
7. C.K. Chiang, S.C. Gau, C.R. Fincher, J R., Y.W. Park, A.G. Mac Diarmid and A.J. Heeger, *Appl. Phys. Lett.* 33,18, (1978).
8. J. Kanicki, S.Bone and E. Vander Donckt, *Molec. Crystals liq. Crystals* 83, 319 (1982).
9. H. Shirakawa, E.G. Lows, A.G. Mac Diarmid, C.K. Chiang and A.J. Heeger, *J.chem. soc. Chem. Commun;* 578 (1977).
10. T.A. Skotheim, R.L. Elsenbaumer, J.R. Reynolds, *Hand book of conducting polymers,* 2ed. Marcel Dekker, New york, vol.1-2. , (1998).
11. H.S. Naiwa, *organic conductive molecules and polymers,* John wiley and sons; vol. 2, England (1977).
12. W.J. Feast, J.Tsibouklis, K.L. Pouwer, L.Groenendual, E.W. Meijer, *Polymer* 37, 5017, (1996).
13. J. L. Bredas, R. Silbey, *conjugated polymers,* kluwer, Dordrecht, (1991).
14. K. Y. Law, *chem. Rev.,* 93, 449, (1993).
15. A. Bohnen, H.J. Rader, K. Mullen, *Synth. Met.* 47, 37, (1992).

16. N. F. Colaneri, D.D.C. Bradley, R.H. Friend, P.L. Burn, A.B. Holmes, C.W. Spangler, *phys. Rev.* **B42**, 11670, (1990).

17. J.H. Burroughes, D.D.C. Bradley, A.R. Brown, N. Marks, K.Mackay, R.H. Friend, P.L. Burn, A.B. Holmes, *Nature*, **347**, 539, (1990).

18. U. Satzner, J.B. Lagowski, D.G. Pickup, P.A. Poirier, *Synth. Met.* **96**,177,(1998).

19. W.P. su, J.R. Schrieffer and A.J. Heeger, *Phy. Rev.* **B22**, 2099 (1981).

20. S. Baeriswyl, Helv. *Phys. Acta*, **56**, 639 (1983).

21. J. L. Bredas, J.C. scott, K.Yakushi and G.B. Street, *Phys. Rev.* **B30**, 1023 (1984).

22. J. L. Bredas, *Molec. Crystals Liq. Crystals*, **118**, 49 (1985).

23. J. L. Bredas, B. Themans, J.G. Fripiat, J.M. Andre and R.R chance, *Phys. Rev.* B 29, 6761 (1984).

24. W.P. su, J.R. Schrieffer and A. J. Heeger, *Phy. Rev. Lett.* **42**, 1698 (1979), *Phys. Rev.* B-22, 2099 (1980).

25. M.J. Rice, *Phys. Lett.* A. **71**, 152 (1979).

26. Y.R. Lin-Liu and K. Maki, *Phys. Rev.* **B-26**, 955 (1982).

27. J. Tinka Gammel and J.A. Krumhansi, *Phys. Rev.* **B-24**, 1035 (1981).

28. C. Rebbi, *Sci. Am.* **240**, 92 (1979).

29. J.L. Bredas, R.R. Chance and R. silbey, *Phys. Rev.* **B26**, 58431 (1982).

30. P.V. Wright, *Polymer* 7, 319 (1975). (b) D.E. Fenton, J.M. Parker, P.V. wright, Polymer **14**, 589 (1973).

31. (a) C.W. Tong, S.A. Vansyke, *Appl. Phys. Lett.* **51**,913 (1987).(b) C.W. Tong, S.A. Vansyke, C.H. chen, *J. Appl. Phys*-**65**, 3610 (1989).

32. S. Son, A. Dodabalapur, A.J. Lovinger, M.E. Galvin, *Science* 269, 376 (1995).

33. C. Zhang, S. Hoger, K. Pakabaz, F. wudl; A.J. Heeger, *J. Electron Meter.* 23, 453 (1994).

34. N.C. Greenham, S.C. Moratti, D.D.C. Bradly, R.H. Friend, A.B. Holmes, *Nature,* 365, 628 (1993).

35. Y. Yang, A.J. Heeger, *Appl.Phys.Lett.* 64, 1245 (1994).

36. D. Braun, A.J. Heeger, *Appl.Phys. Lett.* 58, 1982 (1991).

37. D.D. Gebler, Y.Z. Wang, J.W. Blutchford, S.W. Jessen, L. Blin, T.L. Gustafason, H.L. Wang, T.M. Swager, A.G. Mac Diarmid, A.J. Epstein, *J. Appli. Phys.* 78, 4264 (1995).

38. B. Hu, Z.Yang, F.E. Kuratz, *J. Appl. Phys.* 76, 2419 (1994). (b) J. Kido, K.Hongawa, K. Okuyama, K.Nagai, *Appl. Phys. Lett.* 63, 2627 (1993).

39. M. onada, *J.Appl.Phys.* 78,1327 (1995).

40. D. Braun, G. Gustafasson, D. Mc Branch, A.J. Heeger, *J. Appl. Phys.* 72,564 (1992).

41. M. Berggren, G.Gunstafason, O.Inganas, M.R. Andersson, O.Wennerstrom, T. Hjertberg, *Adv. Mater.* 6, 488 (1995).

42. (a) M.Angelopoulos, J.M Shaw, R.D. Kaplan, S. Perreault, J. *Vac.Sci. Technol.,* B7, 1519 (1989). (b) M. Angelopoulos, J.M. Shaw, K.L. Lee, W.S. Huang, M.A. Lecorre, M. Tissier, *J. Vac. Sci. Techno.* B9, 3428 (1991).

43. W.S. Huang, *Polymer* 35, 4057 (1994).

44. T.J. Skotheim, Ed., *Handbook of conducting polymers,* Marcel Dekker, New York, (1986).

45. (a) M.J. Marsella, T.M. Swager, *J.Am.Chem.Soc.* 115,12214 (1993). (b) M.J. Marsella, P.J. Carroll, T.M. Swager, *J.Am.Chem.Soc.* 116,9347(1994).

46. Roncali, *J.Chem. Rev.*,97,173, (1997).

47. S.Higgins, *J. Chem.Soc.Rev.* 26,247, (1997).

48. C.K. Chiang, C.R. Fincher, Y.W. Park, A.J. Heeger, H.Shirakava, E.J. Louis, S.C. Gau and A.G.Mac.Diarmid, *Phys.Rev.Lett.*,39,1098,(1977).

49. H. Shirakawa and S.Ikeda, *Polymer.*,2,231,1971.

50. D.M. Ivery, G.G. Miller, J.M. Sowa, R.L. Shacklette, R.R. Chance and R.H. Baughman, *J.Chem.Phys.*, 71,1506 (1979).

51. A.F. Diaz, K.K. Kanazawa and G.P.Gardini, *J.Chem.Soc.Chem.Commun.*, 635,(1979).

52. A.F. Diaz, A.Martinez, K.K. Kanazawa and M.Salmon, *J.electroanalyt.chem.*130,181,(1980).

53. G.Tourilon and F.Garnier, *J.Electroanalyt.Chem.*135,173,(1982).

54. G.Tourillan and F.Garnier, *J.Electrochem.Soc.*130,2042 (1983).

55. R.J. Waltman, J.Barzon and A.F. Diaz, *J.Phys.Chem.* 87,1459,(1983).

56. J.Oshsawa, K.Kaneto and K.Yoshino, *J.Ap.J.Appl.Phys.*23,L663 (1984).

57. R.J. Waltman, A.F. Diaz and J. Barzon, *J.Phys.Chem.* 88,4343 (1984).

58. Y.Shirota, N, Noma, H.Kaneza and H.Mikawa, *J.Chem.Soc.,Chem.Commun.*, 470 (1984).

59. J.Barzon, S. Mohamand and R.J. Waltman, *IBM Jl.Res.Dev.*27,330,(1984).

60. T. Ohsaka, Y.Ohnuki, N.Oyama, G.Katagiri and K.Kunisako, *J.Electroanal.Chem.*, 161,399 (1984).

61. D .Bhumik, J.E. Mark, *Polym.Prepr.*, 25,260-267, (1984).

62. F .Garnier. Harowitzer, R .Hajlanui, *Syn.Met.*,57,4747- 4754(1993).

63. D .Fichon; Harowitzer, F .Garnier, *Synth.Met.*, 39,125-131, (1990).

64. D .Fichon, XU B, Harowitzer, F. Garnier, *Synth.Met.*,41-43, 463-469, (1991).

65. *Encyclopaedia of Polymer science and Engineering, second edition,* Vol.5, Mark Bikales over Berger Menges John Wiley and Sons Inc., (1986).

66. M.E.O.Lyons, *Electroactive polymers,* Ed;Plenum Press; New York, PP 1-65, (1994).

67. Chien J.C.W. *Polym.Prepr.* 25,262-263, (1984).

68. H. Djellab., M .Armand, D .Delabouglise.*Syn.Met.*,74,223-226, (1995).

69. F .Mohammed, *Synth.Met*,99,149-154, (1999).

70. A.G.M.Diarmid, A.J. Heeger , *Synth.Met.*,1,101,(1979).

71. I.M .Tour., *Ad.Mater.*6,190-198, (1994).

72. H. Shirakawa, E.J. Louis, A.G. MacDiarmid, and A.J. Heeger, *J.Chem.Soc. Chem. Commun.* 662, (1977)...

73. I.Ikemoto,Y.Cao, M.Yamada, H.Kuroda, I.Harada, H.Shirakawa, and S.Ikeda, *Bull.Chem.Soc.Japan* 55,721 (1982).

74. H.Selig, A.Pron, Mdruy, A.MacDiarmid and A.Heeger, *J.Chem.Soc.Chem.Commun.*,1288 (1981).

75. F.Godler, B.Perscheid, G.Kaindl, K.Menke, and S.Roth, *J.Phys.Part C3*, 44,233 (1983).

76. I.Kulszewicz D.Billaud, A.Pron, P.Bernier, and J.Przyluski, *Mol.Cryst.Liq.Cryst.*83,1191 (1982).

77. M.Haleem, D.Billaud, and A.Pron, *Polym.Commun.* 23,1409 (1982).

78. A.Pro.,A.MacDiarmid, and A.J.Heeger, *Mater.Sci.*, 7,313,(1981).

79. H.Sakai, Y.Maeda, T.Kobayashi, and H.Shirakawa, *Bull.Chem.Soc.Japan* 56, 1616 (1983).

80. A.Pron, M.Zagorska, Z.Kucharski, M.Lukasiak, and J.Suwalski, *Mater.Res.Bull.* 17,1505 (1982).

81. A.G. MacDiarmid and A.J.Heeger, *Synth.Met.* 1,101 (1980).

82. L.W. Shacklette, R.L. Elsenbaumer, R.R. Chance, H.Eckhardt, J.E. Frommer, and R.H. Baughman, *J.Chem Phys.* 75,1919 (1981).

83. S.C. Gau, J.Milliken, A.Prem, A.G. MacDiarmid and A.J. Heeger, *J.Chem.Soc.Chem.Commun.* 662 (1979).

84. H.Eckhardt,P.Delannoy, G.Miller, N.Murthy and R.Baughman, *Proceedings of the 12th North American Thermal Analysis Scociety Conference*, (1983).

85. L.W. Shacklette, R.R. Chance, D.M. Ivory, G.G. Miller and R.H. Baughman, *Synth.Met.* 1,307 (1979).

86. T.Yamamoto, K.Sanechika and A.Yamamoto, *J.Polym.Sci.Polym.Lett.*,18,9,(1980).

87. G. Street, T. Clarke, M. Kroumbi, K.Kanazawa, V.Lee, P Fluger, J.Scott and G.Weiser, *Mol.Cryst.Liq.Cryst.* 83,253 (1982).

88. M. Kobayashi, J.Chen, T.C. Chung, F.Morues, A.J. Heeger and F. Wudl, *Synth.Met.* ,77,1984.

89. Y.Kohno. U.Shogo, K.Kaneto, K.Yoshino, and Y.Inuishi, *Technol.Rep.Osaka Univ.* 34,.47 (1984).

90. T.Ito, H. Shirakawa, S.Ikeda, *J.Polym.Sci.Polym.Chem. Ed.*12,11 (1974).

91. H. Naarmann, N.Theophilou, *Synth.Met.* 22,1 (1987).

92. Karpfen, *Phys.Scr.* T1, 79 (1982).

93. H. Eckhardt, *J.Chem.Phys.* 79,2085 (1983).

94. M. Tanaka, H.Yasuda and J tanaka, *Bull.Chem.Soc, Japan* 55,3639 (1982).

95. B. Francois, M.Bernard and J. Andre. *J.Chem.Phys.* 75,4142 (1981).

96. P. Kovacic and Kyriakis, *J.Am.Chem.Soc.* 85,454 (1963).

97. P. Kovacic and J. Ozlomek, *J.Org.Chem.* 29,100 (1964).

98. G.K. Noren and J.K. Stille, *Macromol.Revs.*,5,385 (1971).

99. A.D. Macallum, *J.Org.Chem.* 13,154 (1948).

100. A.D. Macallum, *U.S patent No.* 2,513,188 (June 2 1950) and No. 2,538,941 (January 23,1951).

101. A.G.Mac Diarmid, J.C.Chiang, A.F. Richter, N.L.D. Somasiri, and A.J. Epsterin, *Conducting Polymers* (L-Alcacer, ed.), Pordrecht, ,PP.105-120, (1987).

102. J.L.bredas and R.S.Silbey., *Conjugated Polymers*, Kluwer Academic Publishers, (1991).

103. R.A. Wessling, R.G. Zimerman, *U.S. patent* 3,4,152 (1968).

104. B.R. Hsich, H. Antoniadis, M.A. Abkwowitz, M.Stolka, *Polym.Prep.*(2) 33,414 (1992).

105. F. Papadimitrakopoulos, M.Yan, L.J. Rothberg, H.E. Katz, E.D. Chundross, M.E. Galvin, *Mol.Cryst.Liq.Cryst.* 256,663 (1994).

106. E.M. Genics, G .Bidan, A .Diaz, *J. Electroanaly Chem.*, 149, 101-113,(1983).

107. K.J. Ivin, Olefin metathesis, *Academic Press San Diego*, 1983.

108. J. Margolis, *Conducting Polymers and Plastics*, Chapman and Hal, London 1993.

109. B. Wessling, *Polym.Eng.Sci*, **31**,1200 (1991).

110. S.S. IM and S.W. Byun, *J.Appl.Polym.Sci.* **51**,1221 (1994).

111. Pallab Banarjee, T.K. Mandal, S.N. Bhattacharya and B.M. Mandal, *Proceedings of the international symposium in macromolecules* **674**, (1995).

112. T. Seevananda, S.Palaniappan, S.Seetharaman and Siddaramaiah, *Proceedings of the IUPAC International symposium on Advances in Polymer Science and Technology*, 1983 ,(1998).

113. S.E. Lindsey and G.B. Street, *Synth.Met*, **10**,67 (1984).

114. O.Niwa and T. Tamamura, *J.Chem.Soc.Chem.Commun.*, **817** (1984).

115. J.C.W. Chien, G.E. Wnek, F.E. Karasz, J.A. Hirsch, *Macromolecules*, **14**,479, (1981).

116. W.Deits, P.Cukor, M.Rubner, H.Jopson, *Synth.Met*,**4**,199, (1982).

117. F.Vannice, F.S. Bates, G.L. Baker, P.J. Carroll, G.D. Patterson, *Macromolecules*,**17**,2626, (1984).

118. J.H. Edwards and W.J. Feast, *Polymer* **21**,595 (1980).

119. P.J. Nigrey, A.G. Mac Diarmid and A.J. Heeger, *J.Chem.soc.Chem.commun.*, **594** (1979).

120. B.C. Kim, G.M.Spinkes, Co.O.Too, G.G. Wallace, Y.H. Bac, N.Ogata, *Reactive & Functional Polymers*, **44**, 245-255,2000.

121. Anuar Kassim, Zarina Bte Busar and H.N.M.E. Mahmud, *Proc. Indian Acad.Science(Chem.Sci.)* **114**,155-162,(2002).

122. Komilla Suri, S.Annapoorni and R.P. Tandon, *Bull.Mater Sci.*,24,563-567,(2001).

123. M.A. Junqung, Huihong song, Harry L Frisch, Shahin Maaref, Sam.S.Sun, *J.Appl.Poly. Sci.*,**85**,2287 - 2293,(2002).

124. Chengwei Wang, Zhen Wong, Li. Mengke, Li. Hulin, *Chemical Physics Letters.*, **341**,431-434, (2001).

125. Hong Quan Xie, Yong-Mei Ma, Jun-shiguo *Synthetic metals*,**123**,47-52,(2001).

126. Yannick kieffel, Jean pierre travers, Anne Ermolieff, Denis Rouchon, *Journal of applied polymer science*, **86**, 395-404,(2002).

127. Zhiming Zhang, Zhixiang Wei and Meixiang Wan *Macromolecules*, 35, 5937-5942, (2002).

128. Liu,J.Wan,M.X.*J, Mater.Chem.*,11,404,(2001).

129. Liu J. M.X. Wan, *J. Polym. Sci., Part A: polym.chem.*,39,997, (2001).

130. M.X.Wan, J. Huang, Y.Q. Shen.,*Synth. Met.*,**101**,708, (1999).

131. M.X.Wan, J.Liu, H.J Qiu, J.C. Li., *Synth.Met.*,**119**,71, (2001).

132. H.J.Qiu, M.X . Wan., B.Mathews, L.M .Dai.,*Macromolecules*,**34**,675, (2001).

133. H.J.Qiu, M.X .Wan, Chinere., *J. Polym. Sci.*,**19**,65, (2001).

134. Wan, M.X., Li, J.C. *J. Polym.Sci.,Part A,Polym.Chem.*,**38**,2359, (2000).

135. Palle Swapner Rao, D.N.Sathyanarayana, and S. Palaniappan, *Macromolecular*,35,4988-4996,(2002).

136. D.Mikael Johansson, Liangjun Wang,Tomas Johansson,Olle Inganas,Uang Yu,Gordana Srdanov and Mats R. Aandersson *Macromolecules*,35,4997-5003,(2002).

137. H.H.Tan,K.G.Neoh,F.T.Liu,N.Kocherjinsky,E.T.Kang,*Journal of Applied Polymer Science*,**80**,1-9,(2001).

138. Qingua Zhang,Lianhong Wang,Yanhon Geng, Dajun chen,Xiabin Jing,*Journal of polymer science:Part B:polymer physics, Vol.***40**,2531-2538,(2002).

139. P.Dutta,Sbiswan,M.hesh,S.K.De,S.Chatterjce, *SyntheticMetals*,**122**,455-461,(2001).

140. Roselena Faez,Macro-A,De Paoli, *European polymer Journal*,**37**, 1139-1143, (2001),.

141. Palle Swapna Rao,D.N.Sathyanarayana, *Polymer*,**43**,5051-5058,(2002).

142. C .Thiemann ,Brett,*Synth.Met.*,**123**,1, (2001).

143. Surswah Koul,R.Chandra,S.K.Dhawan *Seniors and Actuators*,B **75**,151-159,(2001).

144. Hiroaki Yohida,Fumio Takei,Norio-Sawatari,*"FUJITSUsci Tech. J."*,**38**,1,39-45,(2002).

145. Sukanta De, A.De, and S.K.De,*14th Annual General Meeting & theme Symposium "Novel polymeric materials , MRSI, Mumbai"*,(2003).

146. S.S.Umare,S.D.Asthaputery,and U.S.waware, *14th Annual General Meeting & theme Symposium "Novel polymeric materials, MRSI, Mumbai"*(2003).

147. H.C.Pant,M.K.Patra,P.Vashistha,K.Manzoor,S.R.vadera and N Kumar , *14th Annual General Meeting & theme Symposium "Novel polymeric materials , MRSI, Mumbai"*(2003).

148. K.G.Princy,Rani Joseph,C.Sudha Kartha and otto van Asselen *14th Annual General Meeting & theme Symposium "Novel polymeric materials , MRSI, Mumbai"*(2003).

149. S.K.Guptha,Ramadhar Singh, Manju Aror and Amarjeet Kaur, *14th Annual General Meeting & theme Symposium "Novel polymeric materials , MRSI, Mumbai"* (2003).

150. Sreeja R,Predeep P and Rosamma Alex, *Proceedings of fifteenth Kerala Science Congress*,P-631-637,(2003).

151. Han Moon Gyu, I m seung soon *J. Appl. Polym. Sci.* **7.1**,2169-2178,(1999).

152. Pinaho Mangali S; Dezotti Marcia, Gorelora Marianna M; Soures Bluma G; *J.Appl.poly.sci.* 71,2329-2334,(1999).

153. Piellichowski K; *J.Them.Anal.Calorim.***54**,171-175,(1998).

154. M.Finzel, M.Hawley & J.Jon, *Polymer Engineering and Science* **31**, 1240-1244,(1991).

155. M. Kakimoto & Y.Imai, *Macromol.chem-rapid comm.* **14**, 481-484 (1993).

156. H.Jullien & H.Valot, *Polymer* **26**, 506-510(1985).

157. G.Phillips, etal*J.Appli.phys.* **69**,899,(1991).

158. Y.Bazaird, S.Breton, S.Tontain & A Gourdenne, *Eur.polym.J.* 24,521 (1988).

159. Y.Bazird and A. Gourdenne, *Eur. Polym.J.*, **24**,873-881 (1988).

160. Bouazizi and A. Gourdenne, *Eur.polym.J.*, **24**,889 (1988).

161. Gourdenne, *Abstracts of papers of the Am.chem.soc.* **196**,79 (1988).

162. P.Kathirgamnathan, *Polymer*, **43**,3105,(1993).

163. J.R. Ellis in *Handbook of conducting polymers* **Vol 1** (Ed.) T.A. Skotheim, PP 501-5, Marcel Dekker, New York (1986).

164. J. Kanicki, *Handbook of conducting polymers*, **Vol. 1**(Ed.) T.A. Skotheim,

pp –544-660, Marcel Dekker, New york(1986).

165. K.L. Nagai and R.W. Rendell, *Handbook of conducting polymers*, **Vol.2** (Ed.) T.A. Skotheim, PP-967-1039, Marcel Dekker New York (1986).

166. A.J. Epstein, *Hand book of conducting polymers*, **Vol.1** (Ed.) T.A. Skotheim, PP-1041-1097, Marcel Dekker, New York (1986).

167. A.J. Epstein etal, *Proceedings of the NATO Advanced research workshop of intrinsically cond. poly.* Burington (1992) (Ed) M.Adissi, pp 165-178, kluwer, Dordrecht (1993).

168. A.J. Burr, *Polymer,* **26**,963,(1985).

169. P.W. Debye, Polarmolecules, 1927, *Dover Publications*, New York (1945).

170. A.R.Von Hippel, *Dielectric and waves,* John Wiley, New York(1995).

171. H.H.S.Javadi et al, *Synth.Met.*,**29**,E.409,(1989).

172. H.H.S.Javadi et al, *Mol.Cryst.Liq.Cryst.*,**160**,225,(1998).

173. Roman Dabek, *Polymer engineering and science*,**36**,(1996).

174. Van-Tan Truong and John G. Teran, *Polymer*,**36**,405-909,(1995).

175. Bozkurt, *Journal of physics and chemistry of solids*, **63**,685-690,(2002).

176. Mohan V. Jacob, Julina Mazierska, kenneth Leong and Jerzy Krupka, IEEE *Transactions on microwave theory and techniques*, (2001).

177. K.T. Mathew et al; *Material letters*, **56**,249-251,(2002).

178. C. Tsonos, L.Apekis, K.Viras, L.Stepunenko, L.Karabanova, L.Sergeeva, *Solid state ionics*, **143**,229-249,(2001).

179. A.K.Jonscher, *Dielectric relaxations in solids*, Chelsea Dielectric, (1983).

180. Z.h. Wang et al, *Phys.Rev.B., Condens.matter*,**43**,5373,(1991)

181. A.Kobayashi, z.Xu, and H.I. Shirakawa, *J.Appl. Phys.*, **72**,5702,(1992).

182. H.W.Helborg, *Phys.Status solid*, (1)**81**,381,(1984).

183. H.Isolato, M.Ashiskoz,H.Stubb, *Synth.Met.*, **48**,313,(1992).

184. D. Maclunes, Jr; M.A. Druy, P.J. Nigrey, D.P. Nairno, A.G. Mac Diarmid and A.J. Heeger. *J.Chem.soc.chem. communi* 316, (1981).

185. W.R. Salaneck, D.T. Clark, E.J. Samuelsen, *Science and Applications of Conducting polymers IOP Publishing*, P135, (1991).

186. A.C. Patridge, P.Harris and M.K. Andrews, *Analyst*, **121**, 1349-1353,(1996).

187. W.R. Salaneck, D.T. Clark, E.J. Samuelsen, *Science and applis. Of conducting polymers IOP publishing*, P52, (1991).

188. D. Draun and A.J. Heeger, *Appl.phys. Lett.*,**58**,1982(1991).

189. James Margolis, *Conductive polymers and plastics*, Chapman and Hall, P121, (1989).

190. Andrew Barlaw, Entone - OMI representative, (1997).

191. Luis Alcacer, *Conducting polymers special applications, D. Reidel publishing company*, P5, (1987).

192. C. Akyel and E. Bilger, *Energy*, **14**,839 (1989).

193. D.R.J. White, *Electromagnetic Shielding Materials and performances*, Don White consultants Inc., (2nd ed.) ,(1980).

194. C.R. Paul, *Introduction to Electromagnetic compatibility*, John Wiley and sons, New York (1992).

195. H.W ott, *Noise Reduction Techniques in Electronic Systems*, John Wiley and Sons New York, (1987).

196. J. Unsworth etal, *J. Intell.Mater.Syst. Struct*,**5**,595 (1994).

197. M.W. Rupich, Y.P. Liu and A.B. Kon, *Mater.Res.Soc.Symp.Proc*, **293**, 163-168.

198. C. Chen and K.Naishadam, South East in 90 New Orleans, *IEEE*,38,(1990).

199. K. Naishadham and P.K. Kadaba, *IEEE Trans. On micron.Theory Tech,* 39,1158 (1991).

200. Kaynak etal., *5.Mater. Sci. Letl* . 13,1121,(1994).

201. H. Naarmann, *Science and Applications of conducting polymers (Ed.)* W. Salaneck and D.T. Clark, 81-92, Adam Hilger (1991).

202. J.Joo and A.J. Epstein, *Appli.phys.Lett* 65,2278,(1994).

203. D. Richardson, Steath, *Salamander Books Ltd,* (1989).

204. E.F. Knott, J.F. Schaeffer and M.T. Tuley, *Radar cross section (2nd ed.),* Artech Honse (1993).

205. H. De Chanterac et al., *Synth.Met.* 52, 183 (1992).

206. F. Legros and A. Fourrler Lamer, *Mat.Res.Bull.*19,1109 (1984).

207. J. Unsworth et al. *J.intell. Mater Syst. Struct.* 3,380,(1992).

208. M. El Kadiri and J.P. Parneix, *Electronic properties of polymers and related compounds springer series in solid state science,* Vol.63, 183-186, Springer Verlag (1986).

209. S. El Atawy and K. Davidson, *J.Chem.Soc. Faruday Trans,* 90-879, (1994).

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 Polymers

1. Natural rubber (NR)

Natural rubber used is solid block rubber ISNR-5 grade obtained from Rubber Research Institute of India, Kottayam, having the Mooney viscosity [ML (1+4)] at 100^{0}C = 85.3. The Bureau of Indian standard (BIS) specifications for this grade of rubber is given below.

1. Dirt content, % by mass, max - 0.05
2. Volatile matter, % max - 1.00
3. Nitrogen content, % max - 0.70
4. Ash content (%) - 0.60

5. Initial Plasticity, P_0, min - 30.00

6. Plasticity retention index, PRI, min - 60.00

2. Polyvinylchloride (PVC)

Polyvinyl chloride used is Emulsion grade having the K value 70.5, supplied by Chemplast, Madras.

2.1.2. *Rubber Chemicals*

1. Zinc Oxide

Zinc Oxide was obtained from Meta zinc Ltd., Bombay. It has the following specifications:

Specific gravity - 5.5

ZnO content - 99.85%

Heat loss (2hrs at 100^{0}C) - 0.5% max.

2. Stearic acid

Stearic acid used in this study was supplied by Godrej soaps Ltd., Bombay and has the following specifications:

Melting point - 50-69^{0}C

Acid number - 185-210

3. Tetra methyl thiuram disulphide (TMTD)

TMTD was supplied by NOCIL, Bombay. It has the following specifications:

Melting point - 136^{0}C

Specific gravity - 1.4

4. CBS

N-cyclo hexyl-2-benzthiazyl sulphonamide (CBS) used in the study is PIL cure CBS supplied by Polyolefins Industries, Bombay, having the following specifications:

Moisture	-	0.5% max
Specific gravity	-	1.27

5. Sulphur

Sulphur was supplied by Standard Chemical Company Pvt. Ltd., Chennai and has the following specifications:

Specific gravity	-	2.05
Ash(%)	-	0.01 max.
Solubility in CS_2(%)	-	98 max.

2.1.3 *Fillers*

1. HAF

High abrasion furnace carbon black (N330) was obtained from M/s. Carbon and Chemicals (India) Ltd., Cochin having a DBP absorption of 105cm^3/100 g and average diameter of 32 nm.

2. Silica

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

2.1.4 *Materials used in the synthesis*

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 °C

Assay(GC) - 99%

Density(g/cc) - 1.02-1.022

2. Pyrrole

Pyrrole used for the synthesis is AR grade, supplied by SISCO research laboratories (P) Ltd., Mumbai, having the following specifications:

Assay(GC) - 98%

Refractive index - 1.507-1.508

Boiling point - 129-131 °C

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. Ferric chloride

Ferric chloride used is AR grade, supplied by S.D.fine - CHEM. Ltd, Mumbai, of molecular weight 162.21 .

5. Cyclohexanone

Cyclohexanone used in the present study is sulphur free, AR grade, supplied by S.D.fine - CHEM Ltd., Mumbai, having the following specifications:

Assay(GC)	-	99%
Wt/ml	-	.945-.947

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.

2.1.5 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 sulfonic acid

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

6. Toluene sulfonic acid

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

2.2 EXPERIMENTAL METHODS

2.2.1 Preparation of different forms of conducting polymers

Conducting polymers are prepared by chemical methods and the semi inter penetrating polymer networks are prepared by the in-situ polymerization technique. Different forms like powder, pellet and film are prepared for the dielectric property measurements.

1. Powder form

The conducting polymers prepared by the chemical method is filtered, washed and dried under drying conditions like room temperature drying (48 hrs.), vacuum drying (at room temperature, 16 hrs.) and oven drying (at 50 - 60 ^{0}C 6 hrs.). It is then tightly filled in a capillary tube, without any free space, for dielectric property measurement.

2. Pellet form

The polymer in the powder form is taken in a die of diameter 5mm and pressed under a hand press into a pellet. The pellet is taken out from the die carefully and the dielectric properties are measured.

3. **Film** form

Film is prepared by pouring a fixed volume of slightly viscous polymer solution over the cleaned petridish, which is kept on a levelled surface. The solution equally spread over the dish and it is kept at room temperature for about 24 hrs for drying. The dried films are used for the study.

4. Sheet form

4.1 Mill Mixing and Homogenization using Mixing Mill

Mixing and homogenization of elastomers and compounding ingredients are done on a laboratory size (15 x 33 cm) two-roll mill at a friction ratio of 1:1.25. The elastomer is given one pass through the nip of (0.002 X 100)". Then it is given two passes through the nip of (0.002 x 10)" and allowed to band at the nip of (0.002 x 55)" after the nerve disappeared. The compounding ingredients are added as per ASTM D 3184 (1980). The band is properly cut from both sides to improve the homogeneity of the compound.

When it is properly mixed, the compound homogenized by passing six times endwise through a tight nip and finally the batch is sheeted out as very thin sheet (2 mm thickness).

4.2 Cure characteristics using Goettfert Elastograph

The cure characteristics of the compounds determined using a Goettfert Elastograph model 67.85. It is a microprocessor controlled rotor-less cure meter with a quick temperature control mechanism and well-defined homogeneous temperature distribution in the die or test chamber. In this instrument, a specimen of definite size is kept in the lower half of the cavity, which is oscillated through a small deformation angle ($\pm 0.2^0$). The frequency is 50 oscillations per minute. The torque is measured on the lower oscillating die half.

4.3 Molding of test specimens

The test specimens for determining the physical properties are molded in standard mould by compression molding in an electrically heated hydraulic press having 30 x 30 cm platens at a pressure of 200 kg/cm^2 in the mould. The rubber compounds are vulcanized up to their respective optimum cure times at specified temperatures. Upon completion of the required cure cycle, the pressure is released and the sheet is stripped off from the mould and suddenly cooled by plunging into cold water. After a few seconds, the samples are taken from the cold water; and stored in a cold dark place for 24 h and are used for the subsequent tests.

2.3 PHYSICAL TEST METHODS

2.3.1 Fourier transform infrared spectroscopy

Fourier transform infra red 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 are taken in 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 ^{0}C/minute. Thermograms are recorded from room temperature to 800^{o}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 is 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, which is either heat absorption (endothermic) or heat emission (exothermic) of the sample per unit time is measured in comparison 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 $5^0C/min$. The sample size is between 7 and 10mg.

2.3.4 Scanning Electron Microscopy

Scanning electron microscope (SEM) is a very useful tool in polymer research for studying morphology. Scanning electron microscope, JEOL JSM-840 model-6211 (Oxford, England) is used to investigate the morphology of powder form of conducting polymers. In this technique, an electron beam is scanned 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 (photo multiplier 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.

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

In the cavity perturbation technique generally rectangular or cylindrical wave-guide 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 for 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 wave guide cavities

The cavity resonators are constructed from brass or copper wave-guides. The S-band rectangular wave-guide cavity resonator is constructed from a section of standard WR-284 wave-guide. For C band cavity, a section of WR-159 wave-guide is used. A section of WR-90 wave-guide is selected for the fabrication of X band resonator. Table 2.1 shows the design details of S, C, and X band rectangular wave guide cavities[2].

Table 2.1:Design parameters of S,C and X band rectangular wave guide cavities.

Dimensions of the cavity(mm)	S band	C band	X band
Length, d	353	165	135
Breadth, a	72	34.5	22.9
Height, b	33.5	15.5	10
Diameter of the coupling hole	12.8	8	5.5
Length of the slot on the broad wall	225	80	43
Width of the slot	4	2.5	1

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.

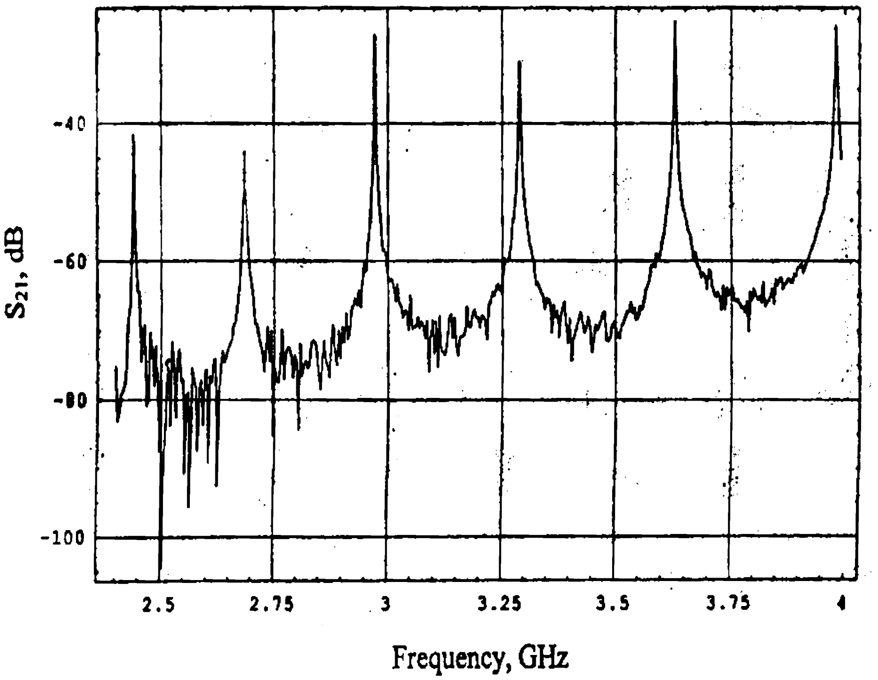


Fig.2.1: Resonance frequency spectrum.

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

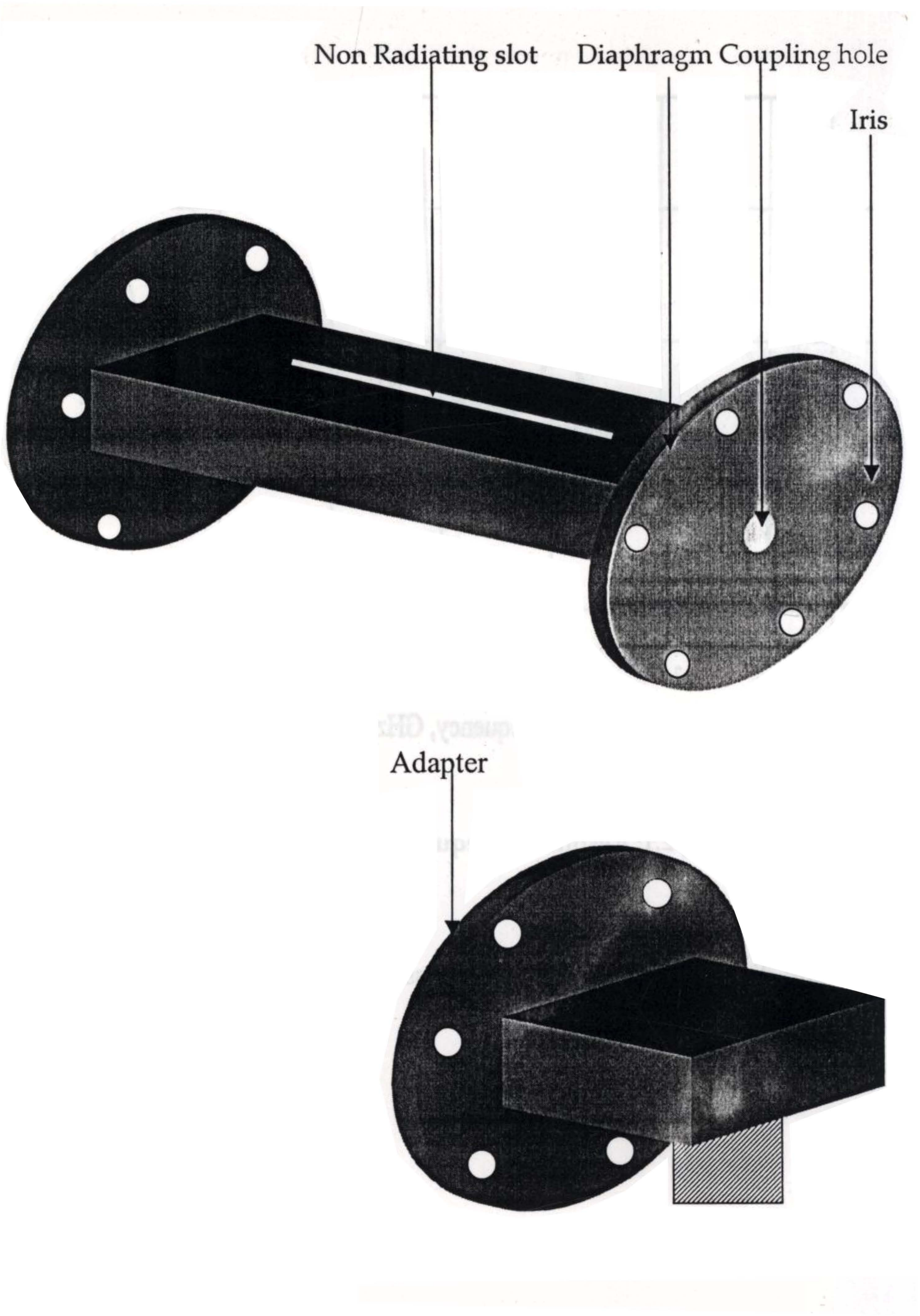


Fig.2.2: Schematic diagram of a typical cavity resonator

Table 2.2 shows the resonant frequencies and the Q factors of the cavities used.

Table 2.2 Resonant frequencies and Q factor values of S, C, and X band cavities.

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
C-band cavity	5.1324	3399
	5.6680	5123
	6.2900	2718
	6.9753	2887
	7.7072	2470
X-band cavity	8.7263	2.90
	9.4725	1635
	10.2849	921
	11.1487	917
	12.0532	993

2.3.5.2 *Set up and theory*

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

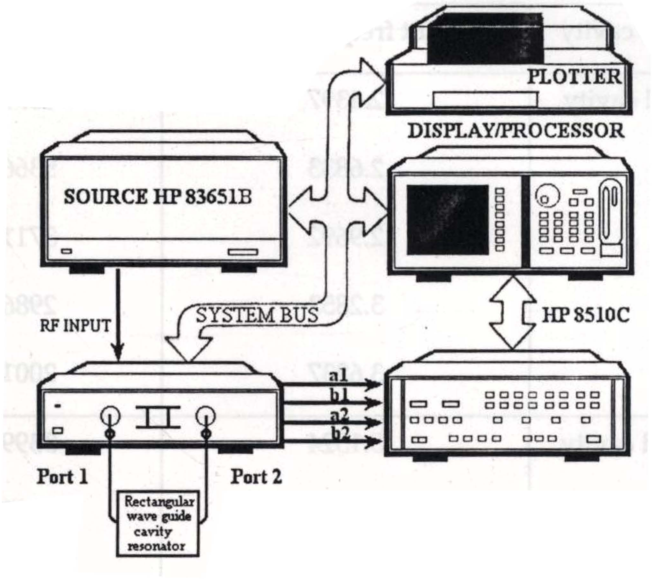


Fig.2.3: Experimental setup

The measurements are done at 25^0 C in S band (2 GHz - 4 GHz), C band (5GHz - 8 GHz) and X band (8GHz -12GHz).

The field perturbation inside the cavity is given by Kupfer et al[4].

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

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. $\bar{\varepsilon}_r$ is the relative complex permittivity of the sample material. Complex frequency shift is related to the quality factor, Q as

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

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,

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

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

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

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

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,

$\tan\delta$ = loss current/charging current = $\varepsilon'' / \varepsilon'$, (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 low frequency conductivity

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

Specifications of the analyzer is shown below:

Frequency - 5 Hz to 13 MHz

Measuring range - .001M Ω to 1.2999 MΩ

with a resolution of 100 μ Ω

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

The resistance of the material at different frequencies (from 10 Hz to 10 MHz) in pellet form is determined from impedence analyzer and then the conductivity is calculated using the equation;

$\sigma = \ell / R \, a$, where

- thickness of the sample

R – Resistance (Ω),

a – area of the sample.

2.4 REFERENCES

1. K. T .Mathew, U. Raveendranath, *Sensors Update*, Baltes, H.; Gopel, W.; Hesse, J. Eds. WILEY-VCH (UK) (1998).
2. U.Raveendranath, *Ph.D. thesis*, Department of electronics, chapter 3,(1996).
3. K.T.Mathew and U.Raveendranath, Waveguide cavity Perturbation method for measuring complex permittivity of water, *Microwave and Optical Technology Letters*, (USA). **Vol.6**, No.2, pp. 104-106,(1993).
4. K .Kupfer, A. Kraszewski, and R.Knochel, *Sensors update* Vol.7 & Microwave sensing of Moist materials, Food and other Dielectrics.Wiley-VCH, Germany,186-209, (2000).
5. Chen. C. Ku; Raimond Liepins, *Electrical Properties of Polymers: Chemical Principles*, Hanser Publishers: Munich, (1987).
6. L. S.Bradford, M.H. Carpentier,*The Microwave Engineering hand book*, Chapman and Hall, London, (1993).
7. C. W. Stephen, H. L.Frederic, *Microwaves made simple: principles and applications* , United States Bookcrafters, Chelsea, (1985).

Chapter 3

STUDIES ON POLYANILINE AND ITS COMPOSITES

3.1 INTRODUCTION

Following the successful synthesis of conducting polyacetylene by Shirakawa et al[1]; electrically conducting polymers have attracted significant attention from all polymer branches with a growing interdisciplinary trend due to various technological applications such as energy storage devices, sensors and strong EMI[2,3] shielding material. Also these materials and very effective for anti-static purposes. From among the large variety of conducting polymers, polyaniline (Pani) has emerged as the most promising one because of its good environmental stability and adequate level of electrical conductivity[4-10]. It is generally recognized that polyaniline is the foremost air stable organic conducting polymer[11] and has a great potential for commercial applications because of its many prominent properties[12]. Interesting applications of polyaniline and its derivatives in the areas of light weight batteries[13], electrochromic displays[14,15], electroluminescent devices[16], electrochemical actuators[17], schottky diodes[18], gas separators[19] and photonic devices[20] have been reported.

The chemical structure of emeraldine base form of polyaniline can be denoted as [(1A)(2A)]n, where 1A and 2A denote (-B-NH-B-NH-) and (-B-N==Q==N-) respectively. Here B denotes a -C_6H_4- ring in the benzenoid form and Q denotes a -C_6H_4- ring in the quinoid form. The emeraldine base form can be fully reduced to the leucoemeraldine $(1A)_n$ and fully oxidized to the pernigraniline $(2A)_n$ forms. Protonation by acid base chemistry results in an internal redox reaction and an associated change in the electronic structure of polyaniline. The conversion from a semiconductor (emeraldine base) to a metal (emeraldine salt) is accomplished by a protonation induced spin unpairing mechanism without any change in the total number of electrons. Thus the electronic structure is converted to a half filled band and a metallic state $[(B\text{-}NH\text{-}B\text{-}NH)^{+\cdot}]_n$ $[A^{-}]_n$, where the positive charge is in the structure, ( ) is the unpaired electron and A^- is the counter ion (eg: Cl^-, NO_3^- etc). In polyaniline electrical properties can be controlled by charge transfer doping and/or protonation. However, two major limitations of polyaniline are the inability to process it by conventional methods and the poor mechanical properties. These limitations can be overcome by preparing conductive blends, composites and interpenetrating polymer networks.

Understanding of transport mechanisms in conducting polymers and the potential use of it as EMI shielding and absorbing materials have encouraged the study of dielectric behaviour at high frequencies. Nagai and Rendell[21]have summarized the theoretical and experimental aspects of a.c conductivity and dielectric relaxation of polymers. Some studies on dielectric behaviour of conducting polymers at microwave frequencies are also reported[22-26].

In this chapter we report the studies on the synthesis, characterisation, and degradation of polyaniline and its dielectric properties at the microwave frequencies. The effect of drying conditions and dopants on the microwave properties are elaborated. To improve the processability, conductive semi inter penetrating polymer networks based on polyaniline-polyvinyl chloride (Pani-PVC) are prepared in various forms like powder, pellet and film and its properties are studied at the microwave frequencies. Cavities operating at S, C, and X bands are used for the study of film samples. In cavity perturbation technique for accuracy of results,the volume of the sample should be less than 1/1000th of the volume of the cavity. Because of this size limitation, the measurements on powder and pellet samples are conducted in the S band only. Also, a report of the preparation of polyaniline - natural rubber semi interpenetrating networks and its dielectric properties in the S band is given. An initial study on the conductivity of polyaniline and its SIPN with polyvinyl chloride of optimised composition in the low frequency region of 10 Hz to 10 MHz, is also reported.

PART I

3.2 STUDIES ON POLYANILINE.

Similar to the other conducting polymers like polyacetylene, polypyrrole and polythiophene, polyaniline is also an insulator in its undoped state. It becomes a good conductor only after doping, which causes the delocalization of charge and spin along the backbone of the polymer. The reversible proton doping and the high conductivity of polyaniline can be utilized in microwave technology for various applications such as coating in reflector antennas, coating in electronic equipment's, frequency selective surfaces, EMI material, beam steering antennas in radar etc. Eventhough there are many studies on the behaviour of poly aniline in the d.c field, those in the a.c field are very rare. Hence it is decided to investigate the various dielectric properties of polyaniline in the microwave frequencies with the aim of utilizing the results for microwave applications. The influence of various forms of polyaniline, the effect of various drying conditions and dopants on its dielectric properties are taken up for the study.

3.2.1 EXPERIMENTAL

- ***Preparation of Polyaniline***

Chemical oxidative polymerization[27] of aniline is carried out using ammonium per sulphate as initiator in the presence of 1M HCl at 0-5^{0}C. The reaction is carried out for 4 hrs. Polyaniline is also prepared at room temperature. The polymer formed is dried under different conditions such as room temperature (for 48 hours), under vacuum (for 16 hours), in oven (at 50 - 60^{0}C for 6 hours. The polyaniline is dedoped (treating polyaniline with ammonium hydroxide for 24 hrs) and then it is doped with different dopants like sulphuric acid, nitric acid, perchloric acid, Toluene sulphonic acid and Camphor sulphonic acid. Also the effect of amount of HCl dopant on the dielectric properties are evaluated.). The dielectric properties of these samples are measured using cavity perturbation technique.

3.2.2. RESULTS AND DISCUSSION

(a) Effect of polymerization condition on dielectric properties

Figure 3.1 shows the dielectric loss and conductivity` of polyaniline prepared at 0-5^{0}C and room temperature (28^{0}C) at 2.97 GHz. It is clear from the figure that the dielectric loss and conductivity are higher for polyaniline prepared at room temperature. 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[28] 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. When the polymerization temperature of aniline is increased head to head sequence of polyaniline is more compared to head to tail sequence. This will induce a steric hindrance with a slight rotation of the two neighbouring cycles as a consequence of this constraint. The effect of this rotation is a weaker overlap of π orbitals and therefore weaker delocalisation of electrons along the chain. This will leads to a high intrachain phenomenon and it will increases the dielectric loss[29]. Therefore polyaniline prepared at room temperature (28°C) gives higher dielectric loss.

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.

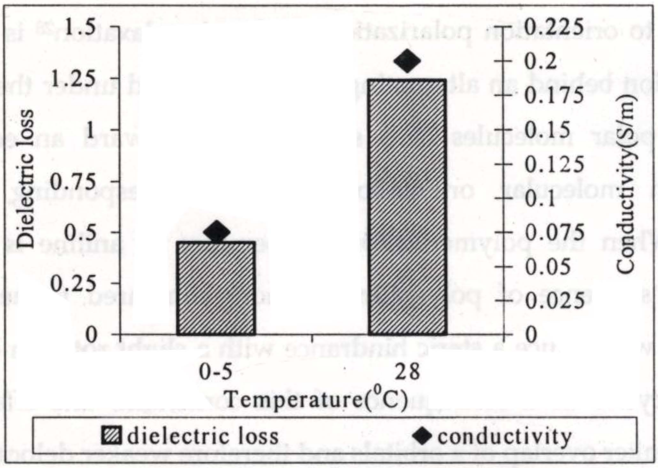


Fig. 3.1: Effect of preparation condition on dielectric loss and conductivity at **2.97 GHz.**

(b) Effect of different dopants on dielectric properties

1. Dielectric loss(ε") and conductivity(σ)

Figure 3.2 and 3.3 shows the effect of different dopants on dielectric loss and conductivity of the material respectively. It is clear from the figures that the dielectric loss and conductivity are greater for HCl doped polyaniline. In the microwave field the dielectric loss and conductivity occurs due to the dipolar polarization under the influence of an a.c. field. 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[30]. 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. Since the conductivity is directly related to the dielectric loss factor the conductivity is also higher for HCl doped samples. Also in the case of HCl dopant, the doping is not diffusion limited and the counter anion (Cl^-) is homogeneously distributed in the material[31].

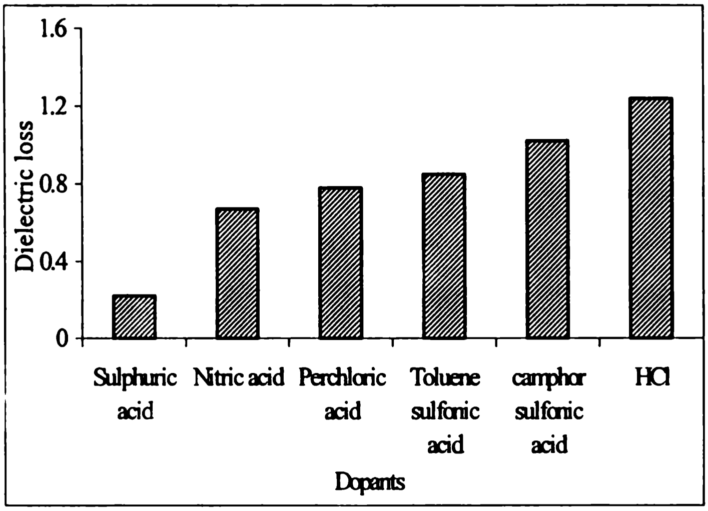


Figure 3.2: Effect of different dopants on dielectric loss at 2.97 GHz.

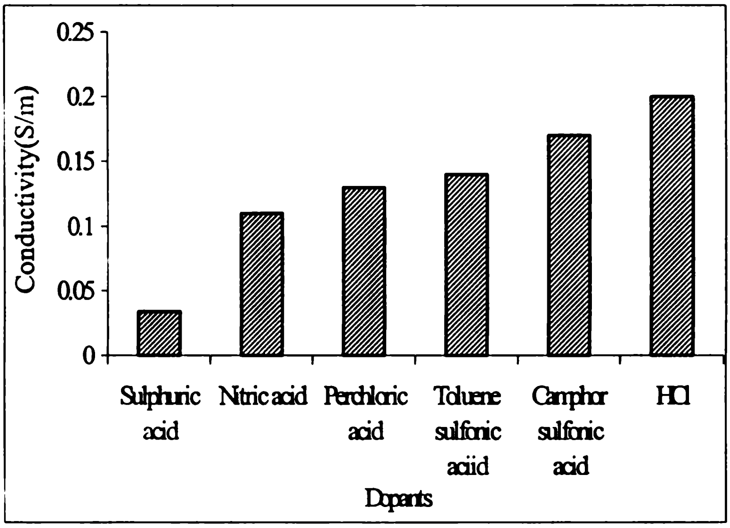


Fig. 3.3: Effect of different dopants on conductivity at 2.97 GHz

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 HCl doped sample is high compared to 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[32]. 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[29].

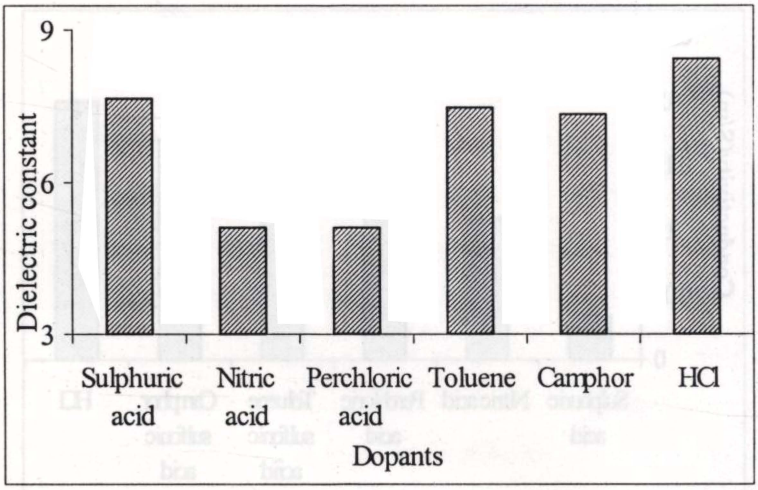


Fig. 3.4: Effect of different dopants on dielectric constant at 2.97 GHz.

3. Dielectric heating coefficient(J)

Figure 3.5 shows the effect of different dopants on the dielectric heating coefficient[33] of polyaniline. It is clear from the figure that the dielectric heating coefficient is minimum for HCl doped sample. The dielectric heating coefficient is inversely related to the dielectric loss factor and hence the HCl doped samples shows the minimum value. The higher the heating coefficient the poorer is the heating property.

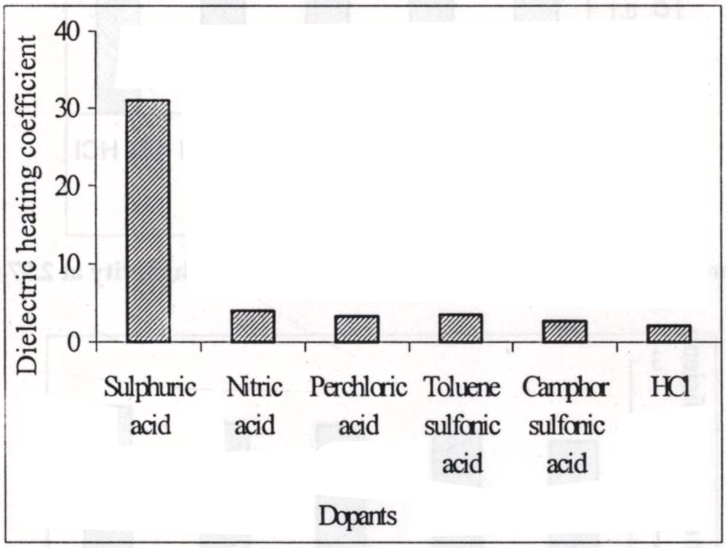


Fig.3.5: Effect of different dopants on dielectric heating coefficient at 2.97 GHz.

Considering these properties the HCl dopant can be optimally selected for further studies.

(c) Effect of different molar concentrations of dopants on dielectric properties

Figures 3.6 and 3.7 shows the variations of conductivity and dielectric heating coefficient at 2.97GHz of samples doped with different molar concentrations of HCl respectively.

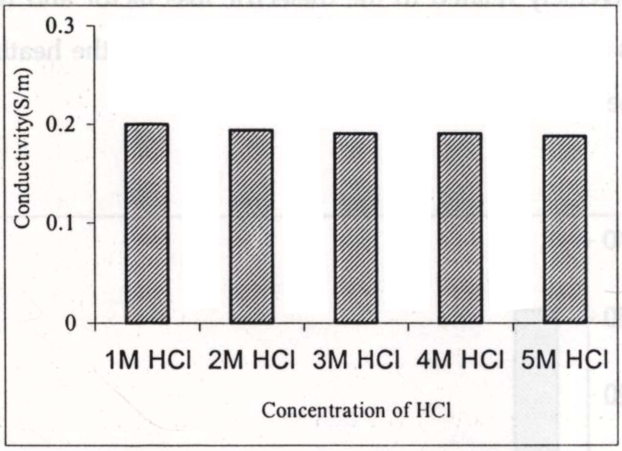


Figure 3.6: Effect of concentration of HCl on conductivity at 2.97 GHz.

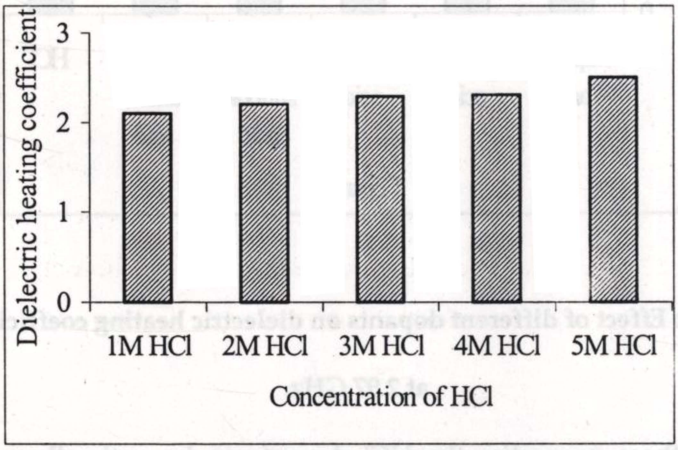


Fig.3.7: Effect of concentration of HCl on dielectric heating coefficient (2.97 GHz).

The figure 3.6 indicates that the conductivity is not much influenced by the molarity of HCl. The 1 M HCl is enough to produce the maximum conductivity in the microwave frequencies. The dielectric heating coefficient is also not much influenced by the molar concentrations of HCl(fig.3.7) and therefore 1 M HCl is optimized for further studies.

(d) Effect of drying conditions on the dielectric properties of polyaniline in various forms

1. Dielectric loss and Conductivity

The variation of dielectric loss of polyaniline powder samples at different drying conditions with frequency at the S band is shown in fig 3.8. The dielectric loss is found to increase with frequency. The dielectric loss at S band is due to the free charge motion within the material[34, 35].

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 3.9 shows the variation of conductivity of polyaniline with frequency. The real part of complex conductivity (σ') is generally considered as a.c conductivity[36] 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.

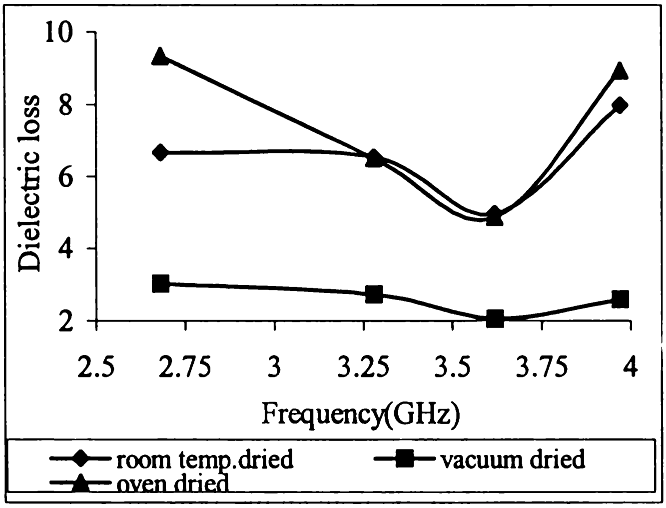


Fig 3.8 : Variation of dielectric loss with frequency.

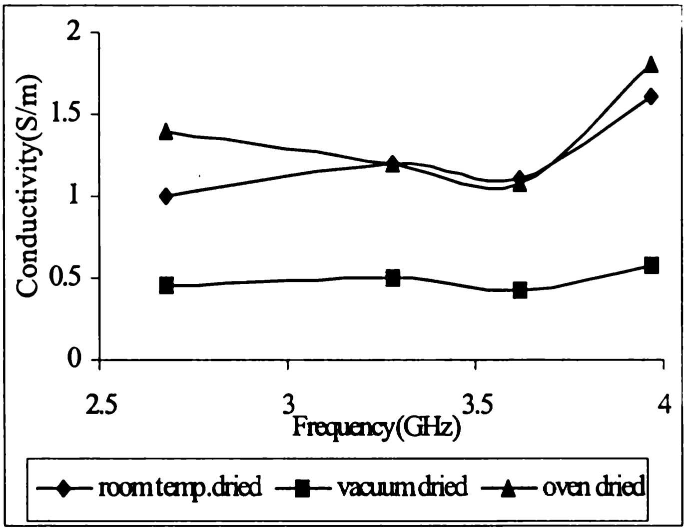
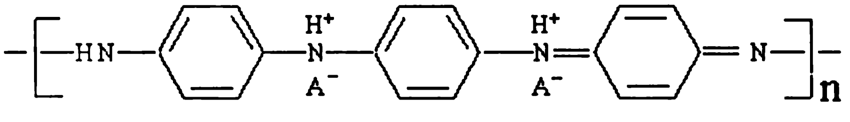


Fig. 3.9: Variation of conductivity with frequency.

In Polyaniline, protonation leads to the formation of radical cation by an internal redox reaction which causes reorganization of electronic structure to give semiquinone radical cations. The degree of protonation and the electronic conductivity thus become a function of dopant concentration.



STRUCTURE OF CONDUCTING POLYANILINE

From this study it is evident that there is a loss of dopant molecules under room temperature and vacuum, which reduces the dielectric loss and hence conductivity. This could be confirmed by the IR spectra of the samples. Figure 3.10, Figure 3.11 and Figure 3.12 shows the IR spectra of oven dried, room temperature dried, and vacuum dried powder samples respectively.

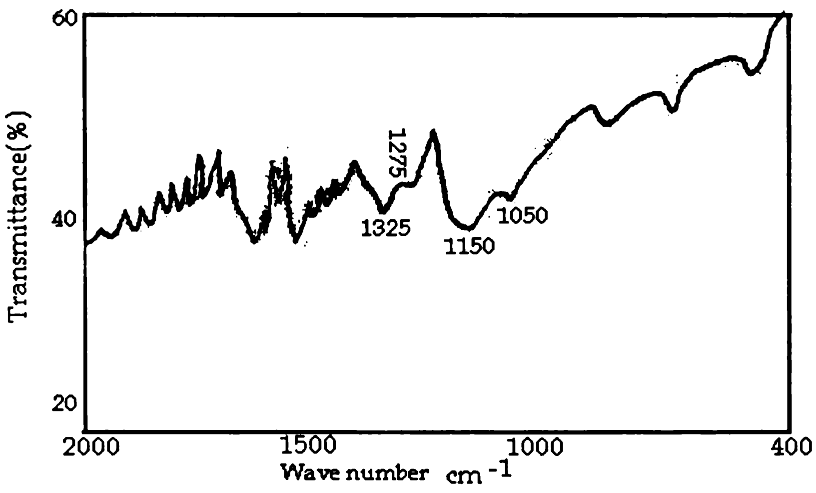


Fig.3.10: IR Spectrum of oven dried Pani.

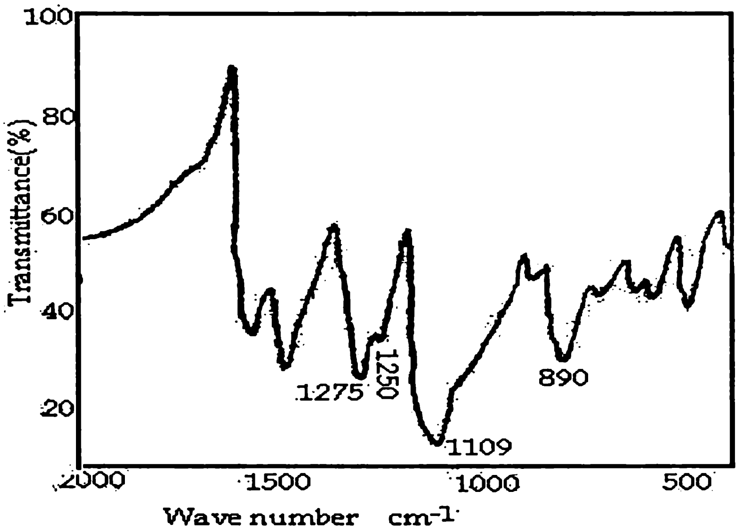


Fig.3.11: IR Spectrum of room temperature dried Pani.

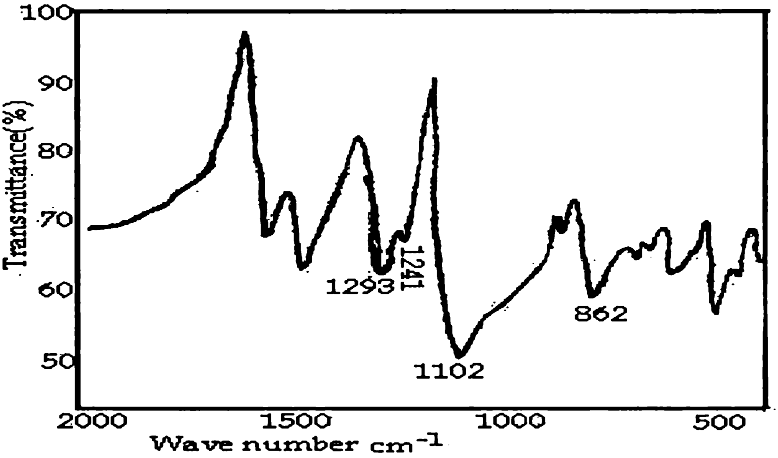


Fig.3.12: IR Spectrum of vacuum dried Pani.

In the IR spectra of the oven dried sample, the principal absorption at 1150 cm^{-1} indicates the presence of Pani-HCl[37]. The absorption at 1325, 1275, 1150, 1050 cm^{-1} are shifted to 1297,1250, 1109.56, 890 cm^{-1} respectively in the case of room temperature dried sample. It is shifted to 1293.94, 1241.8, 1102.57, 862 cm^{-1} respectively in the case of vacuum dried sample. The low frequency shifts can be attributed to the deprotonation of polyaniline salt [38].

2. Dielectric constant

The variation of real part of complex permittivity (dielectric constant) with frequency for powder samples of different drying conditions is shown in figure 3.13.

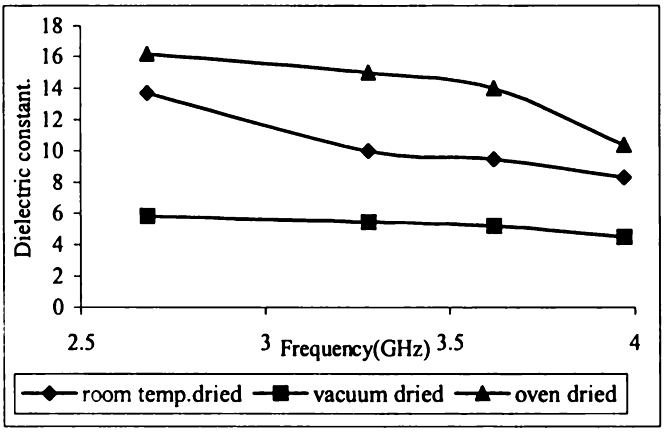


Fig. 3.13: Variation of dielectric constant with frequency for powder samples.

The polarization in the microwave region is caused by the alternating accumulation of charges at inter face due to the presence of dopants, leading to orientation polarization. When the frequency is increased, due to the rotational displacement of molecular dipoles under the influence of alternating field dielectric relaxation occurs and this may leads to a decrease in dielectric constant[39]. The dielectric constant is also found to depend on the drying condition. The oven-dried sample shows the highest value as shown in figure 3.13.

3. Loss Tangent(tan δ)

Figure 3.14 shows the variation of loss tangent of polyaniline samples with frequency.

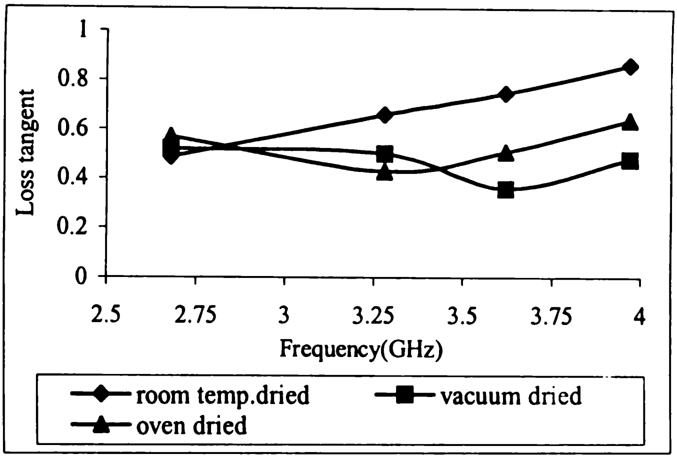


Fig. 3.14: Variation of loss tangent with frequency.

Loss tangent is the angle δ between the vector for the amplitude of the total current and that for the amplitude of charging current and the tangent of this angle is the loss tangent[32]. As it is directly related to the dielectric loss. Therefore the loss tangent also shows the same behaviour as that of dielectric loss.

4. Dielectric heating coefficient(J)

Figure 3.15 shows the variation of dielectric heating coefficient with frequenc The heating coefficient is inversely related to the loss tangent and hence decreases with increase in frequency. As the heat generation in polymers due to relaxation loss, the efficiency of heating of a polymer is compared l means of a heating coefficient[39].

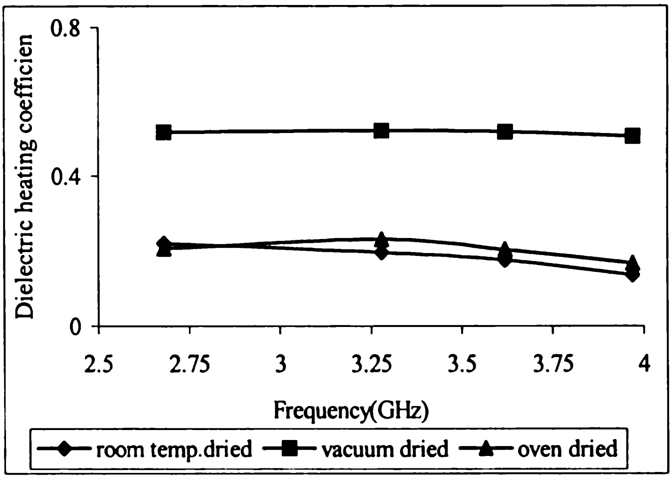


Fig. 3.15: Variation of dielectric heating coefficient with frequency.

Since the dielectric properties of oven dried samples are better, it is selected i study the dependence of absorption coefficient and penetration depth c frequency.

5. Absorption coefficient and penetration depth

Figure 3.16 shows the variation of absorption coefficient with frequency. Tl absorption coefficient is directly related to the dielectric loss factor an therefore it shows the same behaviour as dielectric loss.

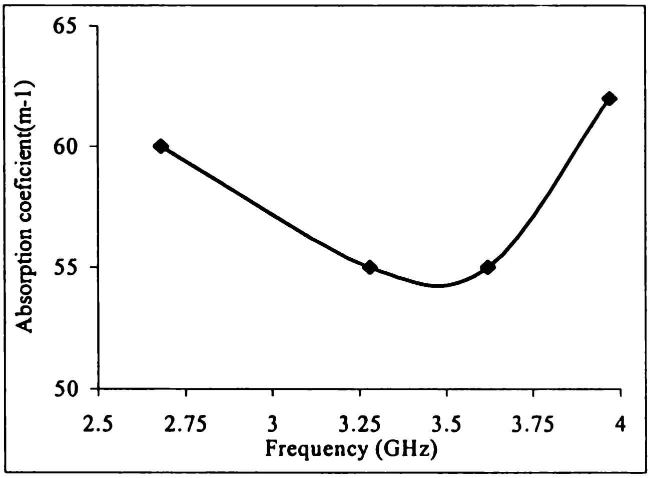


Fig.3.16 : Variation of absorption coefficient with frequency.

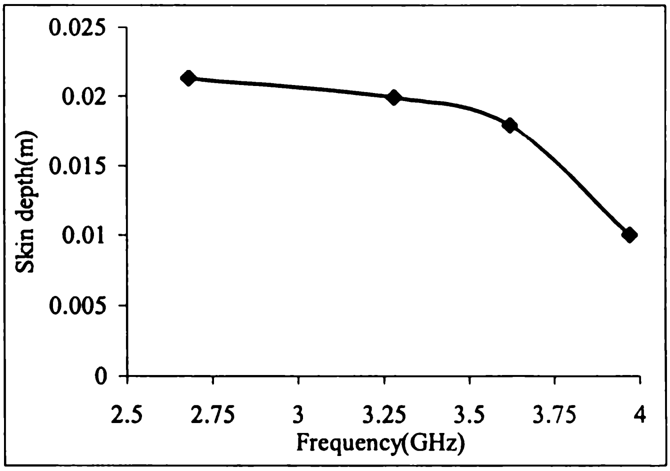


Fig. 3.17: Variation of skin depth with frequency.

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, the dielectric materials can be classified in terms of this parameter indicating transparency of waves passing through it[40].

The variation of skin depth with frequency is given in figure 3.17. 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[41], it can be applied to a conductor carrying high frequency signals. The self-inductance of the conductor effectively limits the conduction of the signal to its outer shell and the shell's thickness is the skin depth, which decreases with increase in frequency.

(e) Dielectric properties of pellet samples

The dielectric properties of pellet samples at 2.97 GHz frequency is shown in table 3.1. It also shows the same behaviour as that of powder samples. In the case of pellet samples the dielectric loss, absorption coefficient, dielectric constant and conductivity are higher and penetration depth , dielectric heating coefficient are lower for the oven dried samples when compared to room temperature dried and vacuum dried samples. A typical graph of conductivity of pellet samples with frequency is shown in the figure 3.18.

Table 3.1: Dielectric properties of pellet samples at 2.97 GHz.

	Room Temp. Dried	Vacuum Dried	Oven Dried
Dielectric loss	0.452	0.171	0.94
Conductivity(S/m)	0.072	0.027	0.15
Dielectric constant	11.32	8.09	11.18
Dielectric heating coefficient	11	40.34	3.6
Absorption coefficient(m^{-1})	4.02	1.8	8.41
Skin depth(m)	0.25	0.555	0.118

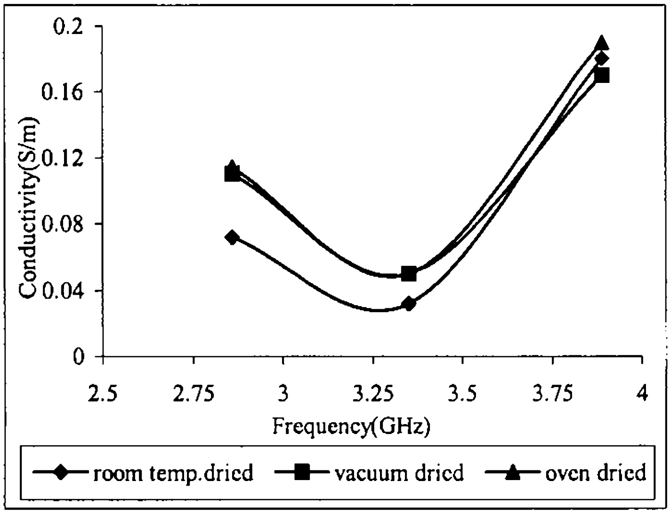


Fig. 3.18: Variation of conductivity of polyaniline pellet samples with frequency.

(f) Comparison of dielectric properties of powder and pellet samples

On comparing the dielectric properties of powder and pellet samples the powder samples shows better dielectric properties as given in table 3.2. It may be due to the higher dilution of the powder matrix. As per the Arrhenius theory the higher the dilution of matrix the greater is the conductivity and therefore the powder samples have more conductivity compared to pellet samples.

Table 3.2: Comparison of powder and pellet samples of Pani at 2.97 GHz.

Property	Powder	Pellet
Dielectric loss	8.95	1.24
Conductivity(S/m)	1.8	.205
Dielectric constant	9.6	8.4
Dielectric heating coefficient	0.3	2.1
Loss tangent	0.51	0.15
Absorption coefficient(m^{-1})	62	13.2
Skin depth(m)	0.01	0.08

Also this may be due to the evolution of dopants during pelletization and it can be confirmed by the IR spectra. Figure 3.19 shows the IR spectra of oven dried powder and pellet samples. In the IR spectrum of pellet sample the absorption peaks are shifted to 1315, 1160, 1075, 1025 cm^{-1} respectively from

1325, 1275, 1150, 1050 cm^{-1} of powder sample, which indicates the loss of dopant molecules[42].

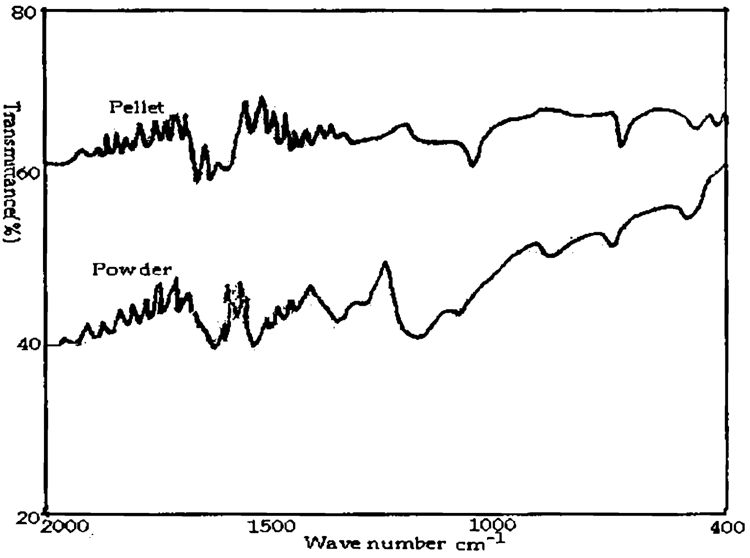


Fig.3.19: IR Spectrum of pellet and powder form of Pani.

The powder samples are more capable of producing a dipolar polarization under the influence of an a.c. field due to its dilution and hence showed an increased the dielectric constant. These samples show a low heating coefficient, since the heating coefficient is inversely related to the loss tangent. The absorption coefficient is high and the skin depth is less for powder sample.

PART II

3.3 STUDIES ON POLYANILINE-POLYVINYL CHLORIDE SEMI INTERPENETRATING POLYMER NETWORKS (PANI: PVC SIPN)

3.3.1 Pani: PVC SIPN's In Powder and Pellet Form

3.3.1.1. 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[1]. 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.

Incorporation of conducting polymer in to a host polymer substrate forming a blend, composite or inter penetrated bulk network has been widely used as an approach to combine electrical conductivity with desirable physical properties of polymers[43,44]. Polyaniline is considered as one of the most promising candidate for the fabrication of conductive blends / composites with industrially important class of polymers[45].

Interpenetrating network conducting composite result through in-situ polymerization of monomers of conducting polymers inside the matrices of the conventional linear polymers. It can be by chemical or electrochemical polymerization method. The electrochemical method uses[46,47] an electrode coated with conventional polymers. In chemical polymerisation[48,49,50], oxidizing agents such as ferric chloride or cupric chloride is incorporated into the polymer film. The film is then exposed to the monomer vapour or to a solution of the monomer in an appropriate liquid.

The dc and ac conductivity of polyaniline / polyvinyl-alcohol blends[51] and polyaniline and zinc sulfide composites were studied in the microwave field[52]. There are a number of papers dealing with this composite. Banerjee and Mandal[53,54] 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[55,56]. 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[57]. The electrochromic behaviour of polyaniline-PVC composite films with structural changes in polyaniline, using FTIR studies were also reported[58]. Kaiser et al[59] have recently reported the conductivity and thermopower data for polyaniline blends with polyvinyl chloride, which showed an increase in conductivity at lower temperature.

In this part of the study we report the synthesis, characterization and dielectric properties of polyaniline (Pani)-polyvinyl chloride (PVC) semi interpenetrating networks in powder and pellet forms.

3.3.1.2 EXPERIMENTAL

- **Preparation**

Chemical oxidative polymerization of aniline is carried out using ammonium per sulphate as initiator in the presence of 1M HCl and emulsion grade polyvinyl chloride. The polymerization is carried out for about 4 hrs. at room temperature. It is then filtered, washed and dried under different conditions like room temperature (48 hrs.), in oven (at 50-60°C for 6 hrs.), in vacuum (at room temperature, for 16 hrs.). Different compositions of Pani:PVC SIPN's, say, 4:1, 2:1, 1:1, 1:1.5, 1:2, 1:2.5 are prepared using the above procedure and the microwave properties are measured.

As the conductivity is the decisive parameter which determines the major class of applications of conducting polymers, the conductivity of different compositions of Pani:PVC SIPN' of powder and pellet forms are compared to optimise the drying conditions.

3.3.1.3 RESULTS AND DISCUSSION

(a) Optimisation of drying condition

The comparison of conductivity of different dried SIPN's in powder and pellet forms are given in the figures 3.20 and 3.21 respectively. It is clear that the oven-dried samples show higher conductivity when compared to room temperature dried and vacuum dried samples as in the case of Pani alone. The reason is same as explained in Part I.

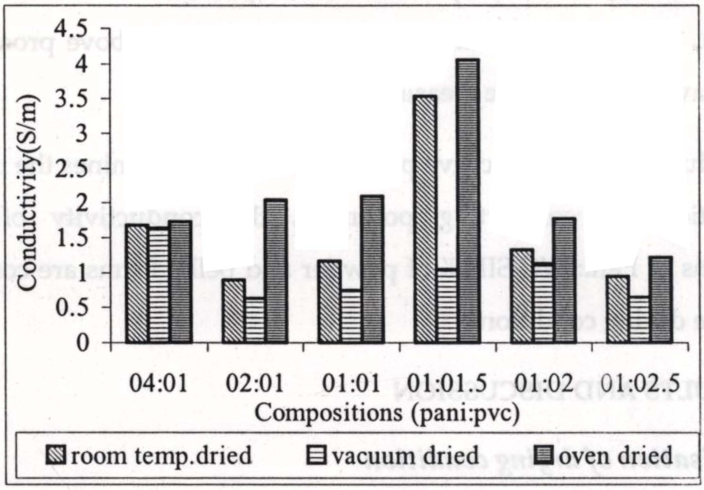


Fig.3.20: Conductivity of different dried Pani : PVC SIPN's(powder form) at 2.97 GHz.

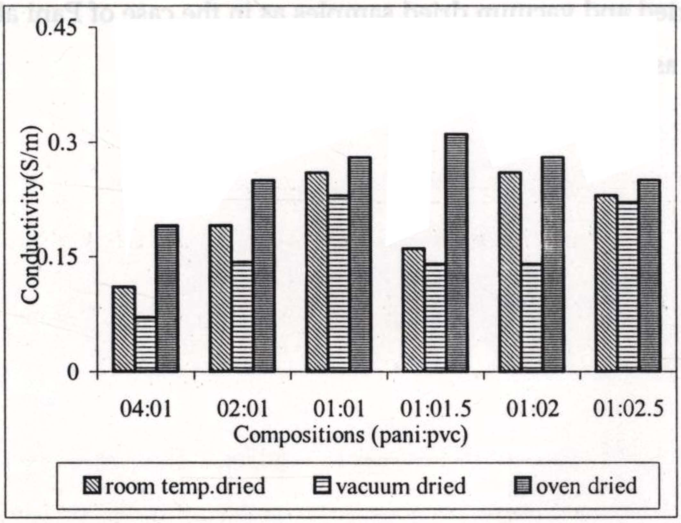


Fig.3.21: Conductivity of different dried Pani : PVC SIPN's(pellet form) at 2.97 GHz.

(b) Variation of dielectric properties with frequency

1. Dielectric loss

Fig 3.22 shows the variation of dielectric loss of different proportions of pellet form of Pani :PVC SIPN's in pellet form with frequency. It is clear from the figure that the dielectric loss is high at high frequency for all proportions. Here also there is a dip in the middle frequency as in the case of polyaniline.

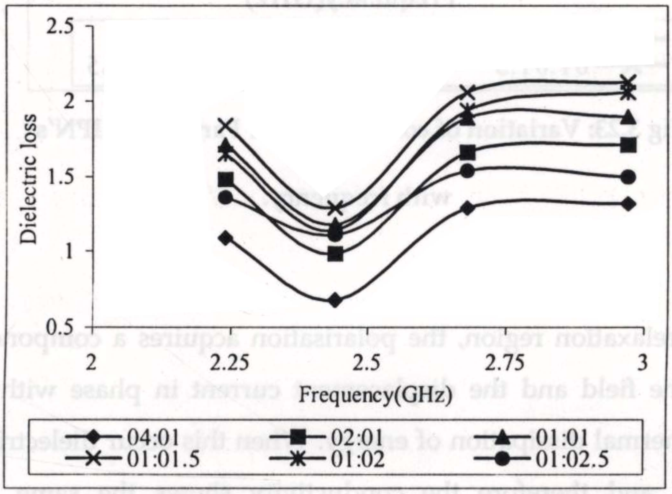


Fig. 3.22 :Variation of dielectric loss of Pani:PVC SIPN's with frequency .

2. Conductivity

The conductivity of the different proportions of polyaniline-polyvinyl chloride semi inter penetrating networks is plotted against frequency in figure 3.23. It is clear from the figure that the variation of conductivity is same as that of dielectric loss.

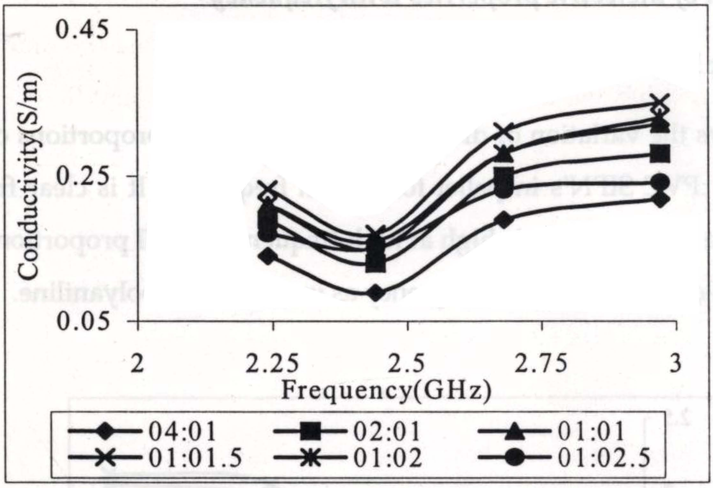


Fig 3.23: Variation of conductivity of Pani:PVC SIPN's with frequency.

At dielectric relaxation region, the polarisation acquires a component out of phase with the field and the displacement current in phase with the field, resulting in thermal dissipation of energy. When this occur dielectric loss will be generated and therefore the conductivity shows the same behaviour (because the conductivity is a direct function of dielectric loss).

3. Dielectric constant

The variation of dielectric constant of pellet samples with frequency is plotted in figure 3.24 .It is clear from the figure that the dielectric constant decreases with increase in frequency as observed in the case of polyaniline. This may be due to the orientation polarization in the microwave field. The higher the polarisability of the material the greater will be the dielectric constant. At sufficiently low frequencies all three types (electronic, atomic and orientation) polarisation can reach the values they would obtain in a steady field. As the frequency of the applied field is increased the polarization has no time to reach its steady field value and the orientation polarization is the first that fails[32].

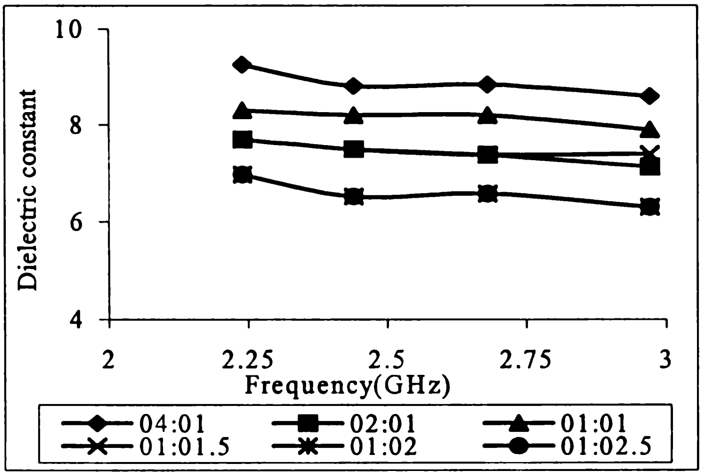


Fig 3.24: Variation of dielectric constant of Pani:PVC SIPN's with frequency

Then the total polarisability falls to $\alpha_T - \alpha_O$, where α_T is the total polarisability & α_O is the polarisability of orientation polarisation. This fall in polarisability, constitute dielectric relaxation, which inturn reduces the dielectric constant.

4. Loss tangent

Since the loss tangent is directly proportional to the dielectric loss factor the variation with frequency is similar to the variation of dielectric loss as shown in the figure 3.25.

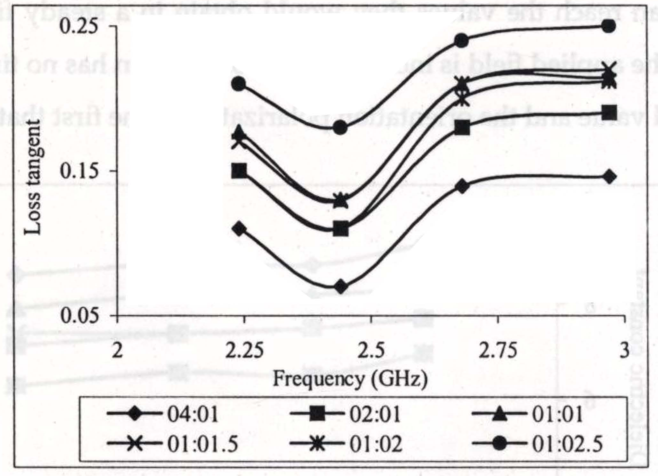


Fig.3.25: Variation of loss tangent of Pani:PVC SIPN's with frequency.

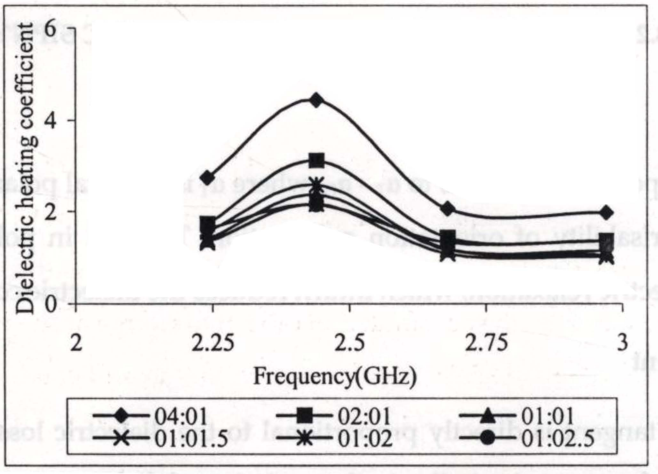


Fig 3.26 :Variation of dielectric heating coefficient of Pani:PVC SIPN's

with frequency.

5. Dielectric heating coefficient(J)

It is observed that the dielectric heating coefficient decreases with increase in frequency as shown in figure 3.26. It is clear from the figure that the SIPN's show very good dielectric heating property, i.e., the dielectric heating coefficient is less, at higher frequencies in all cases.

Tthe powder samples also shows the same trend as that of pellet samples (not shown).

(c) Variation of dielectric properties of SIPN's with compositions

1. Dielectric loss and conductivity

The dielectric loss and conductivity of different proportions of SIPN's in powder and pellet forms are plotted in figure 3.27 and figure 3.28 respectively. It is very interesting that the dielectric loss and conductivity of SIPN's increases with increase in PVC content.

Eventhough, basically PVC is an insulator, the conductivity of the base conducting polymer (polyaniline) increases on adding PVC and it reaches a maximum for 1:1.5 proportion in both cases 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[60]. In the case of polyaniline-PVC SIPN 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

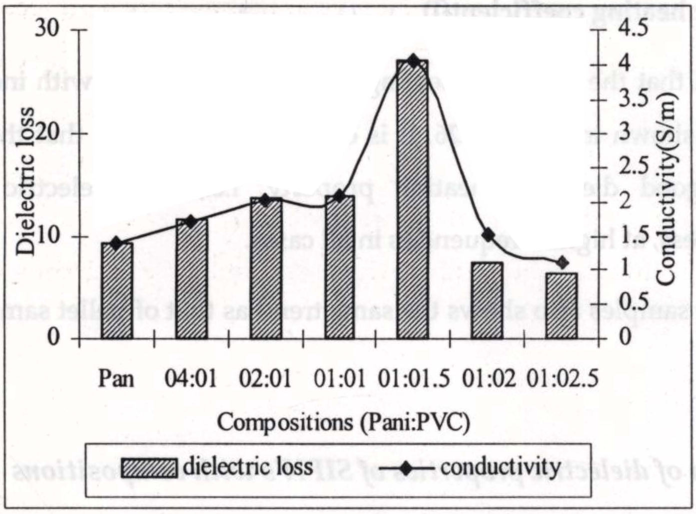


Fig.3.27: Variation of dielectric loss & conductivity with compositions of Pani: PVC SIPN (powder form) at 2.97 GHz.

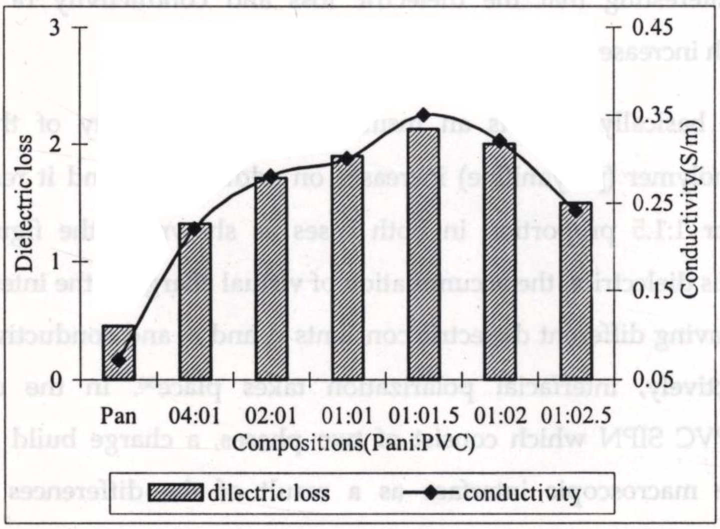


Fig.3.28: Variation of dielectric loss & conductivity with compositions of Pani: PVC SIPN (pellet form) at 2.97 GHz.

geometrical shape of its dispersion[61]. 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 SIPN. The quantity and geometry of the PVC 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: PVC SIPN.

2. Dielectric constant

The variation of dielectric constant with different proportions in powder and pellet forms is plotted in figure 3.29 and 3.30 respectively.

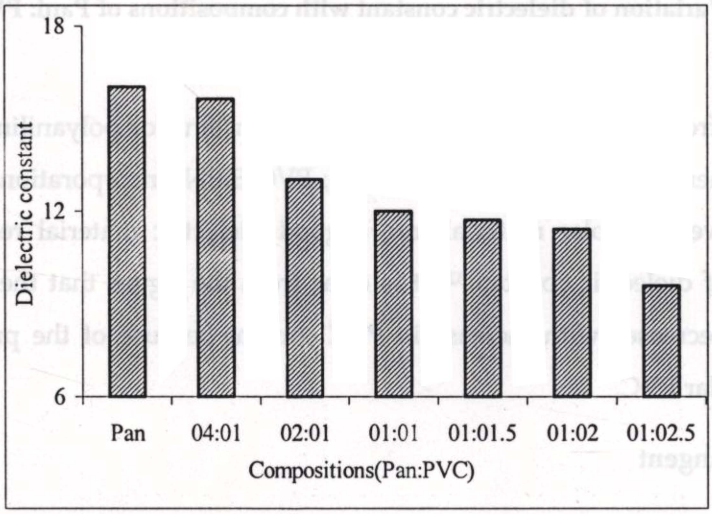


Fig.3.29:Variation of dielectric constant with compositions of Pani: PVC SIPN (powder form) at 2.97 GHz.

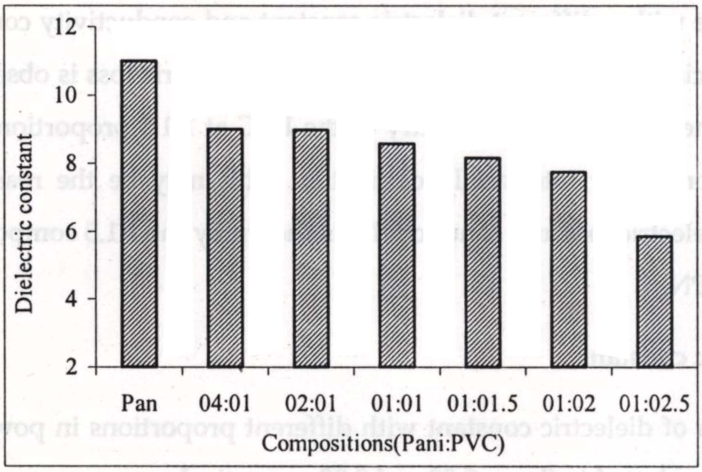


Fig.3.30:Variation of dielectric constant with compositions of Pani: PVC SIPN (pellet form) at 2.97 GHz.

It is clear from the graphs that the dielectric constant for polyaniline alone is much higher when compared to the Pani: PVC SIPN. Incorporation of a non-polar or weakly polar material into a good dielectric material results in a decrease of dielectric constant[32]. It is clear from the figure that the dielectric constant decreases with increase in PVC content because of the presence of weakly polar PVC.

3. Loss tangent

Figure 3.31 and 3.32 shows the variation of loss tangent for different proportions of SIPN's. The loss tangent is directly related to the dielectric loss and hence the loss tangent is higher for 1:1.5 proportion in both powder and pellet form as expected.

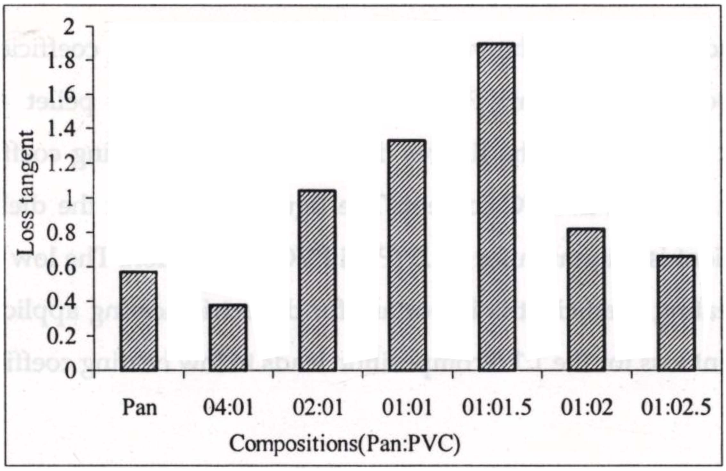


Fig 3.31:Variation of loss tangent with compositions of Pani: PVC SIPN (pellet form) at 2.97 GHz.

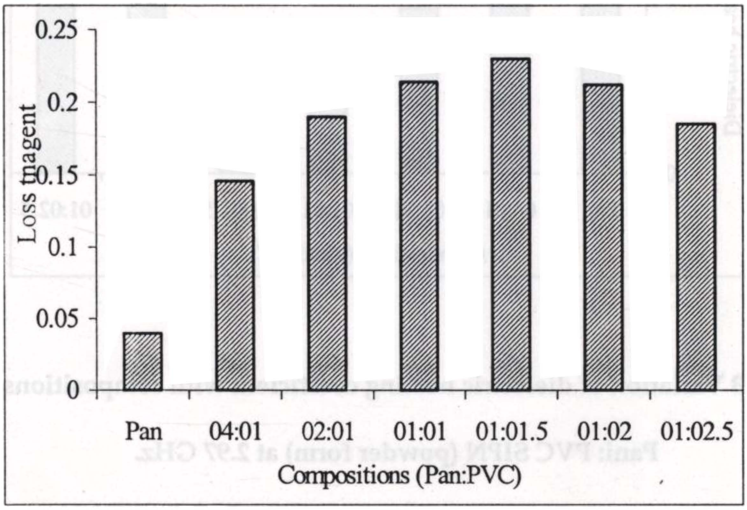


Fig 3.32:Variation of loss tangent with compositions of Pani: PVC SIPN (pellet form) at 2.97 GHz.

4. Dielectric heating coefficient

Figure 3.33 and 3.34 shows the variation of dielectric heating coefficient of different proportions of Pani: PVC SIPN in powder and pellet forms respectively. 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 1:1.5 (Pani:PVC) proportion. The low value of dielectric heating coefficient is important for dielectric heating application. The high tangent loss for the 1:1.5 composition leads to low heating coefficient

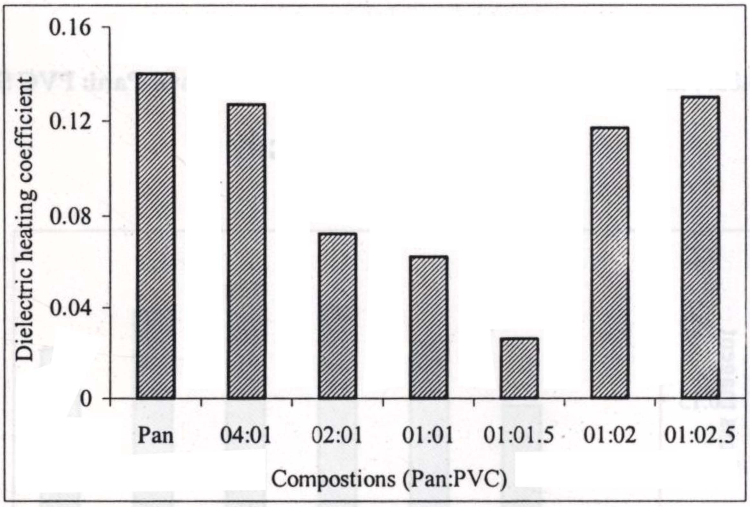


Fig 3.33 Variation of dielectric heating coefficient with compositions of Pani: PVC SIPN (powder form) at 2.97 GHz.

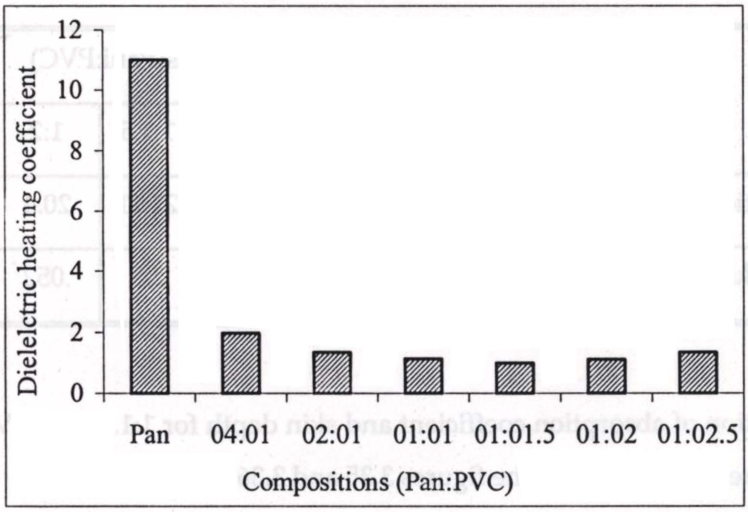


Fig.3.34: Variation of dielectric heating coefficient with compositions of Pani: PVC SIPN (pellet form) at 2.97 GHz.

5. Absorption coefficient and skin depth

The table 3.3 shows the variation of absorption coefficient and skin depth of different compositions of Pani:PVC SIPN in pellet form. 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.

Table 3.3:Absorption coefficient and skin depth of SIPN's at 2.97 GHz.

	Compositions(Pani:PVC)					
	4:1	2:1	1:1	1:1.5	1:2	1:2.5
Absorption coefficient(α_f) (m^{-1})	13.6	17.5	19.6	21.11	20.4	18.7
Skin depth(δ_f)(m)	.07	.06	.055	.05	.052	.06

The variation of absorption coefficient and skin depth for 1:1.5 Pani:PVC SIPN with frequency is shown in the figures 3.35 and 3.36.

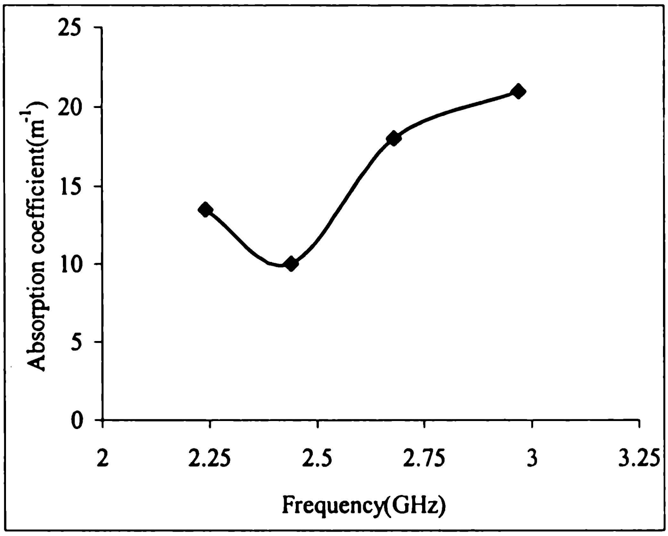


Fig. 3.35 : Variation of absorption coefficient of 1:1.5 Pani:PVC SIPN with frequency.

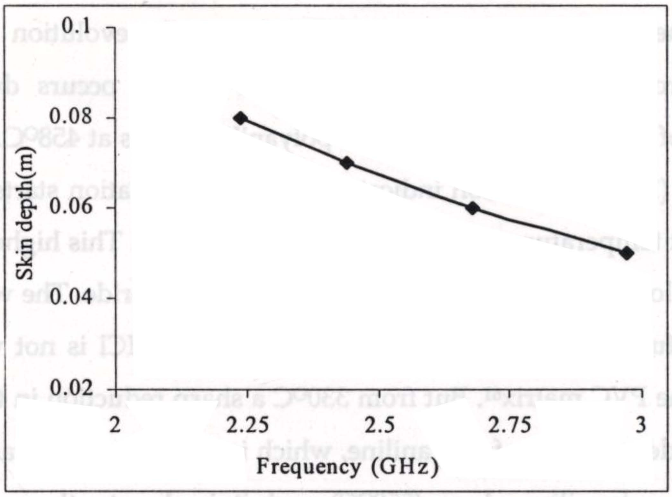


Fig.3.36 : Variation of skin depth for 1:1.5 Pani:PVC SIPN with frequency.

It is clear that the absorption coefficient shows the same behaviour as that of dielectric loss since the absorption coefficient is directly related to the dielectric loss and the skin depth decreases with increase in frequency.

(d) TGA studies

The thermograms of polyaniline alone and polyaniline: polyvinyl chloride SIPN of different proportions like 4:2,1:1.5,1:2 in powder form are shown as figure 3.37. The figure indicates that there is a weight loss of 20% for polyaniline alone due to the evolution of HCl dopant at 240^{O}C. Then about 41% of weight loss at 550^{O}C indicate the degradation of polyaniline chain. In the case of PVC alone (figure 3.38) the degradation starts at 272^O C , but it only 4 %. It may be due to the evolution of HCl. The thermogram of polyvinyl chloride shows a weight loss at 330^O C for about 50 % and above that temperature there is a sharp decrease in the weight loss curve indicates the complete rupture of the material. Considering the thermogram of Pani: PVC (4:1) SIPN, there is a weight loss at 120°C due to the evolution of dopant molecules. From 290°C a sharp reduction of weight occurs due to the degradation of PVC. The degradation of polyaniline starts at 458°C. The TGA of Pani: PVC (1:1.5) proportion indicates that the degradation starts at 350°C and from that temperature a sharp reduction is observed. This higher stability for the initial loss is due to the presence of polyvinyl chloride. The weight loss may be a diffusion-controlled phenomenon where by HCl is not volatilized easily from the PVC matrix[61]. But from 330°C a sharp reduction in the weight indicates the degradation of polyaniline, which is at earlier temperature when compared to polyaniline alone (550°C) and it is due to the presence of polyvinyl chloride. In the case of 1:2.5 proportion also the initial degradation is reduced, i.e., the degradation starts at 260°C and then a sharp decrease is observed.

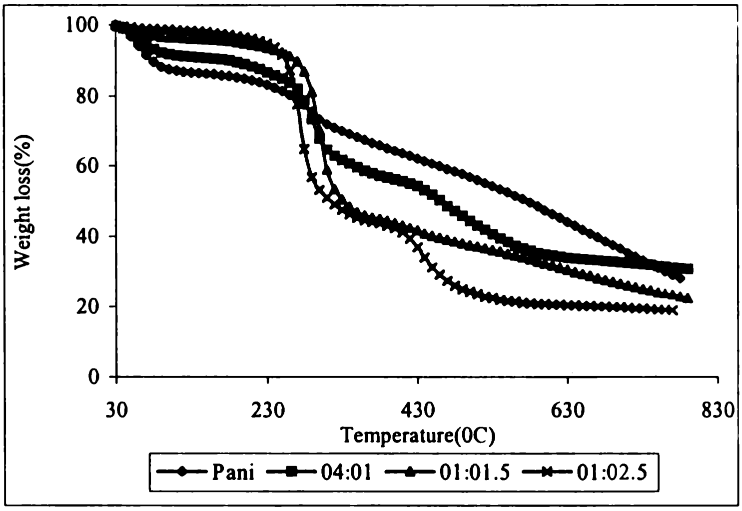


Fig.3.37: TGA thermogram of Pani and its SIPN's

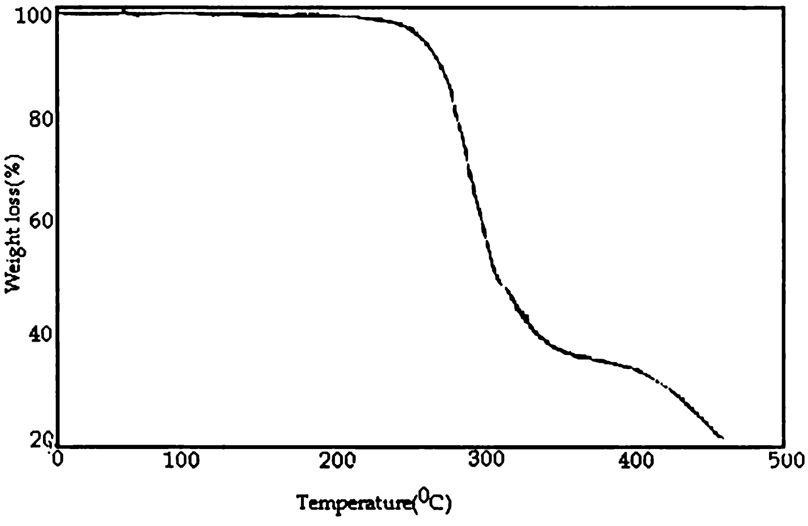


Fig.3.38: TGA thermogram of PVC.

(e) SEM Analysis.

Figure 3.39, 3.40 and 3.41 shows the scanning electron micrographs (SEM's) of polyaniline powder, polyvinyl chloride powder and Pani:PVC (1:1.5) composition. The SEM photograph of polyaniline shows that the chains are loosely packed and having a grain size of 1 µm. In the case of polyvinyl chloride, it shows a globular shape and is thickly packed with a size of 2 µm(fig.3.40). Figure 3.41 shows that the polyaniline is uniformly distributed in the PVC matrix and there is no separate domains for PVC and Pani. It is also clear from this figure that the polyaniline chains are interpenetrated in polyvinyl chloride matrix and it forms a semi interpenetrating networks with PVC.

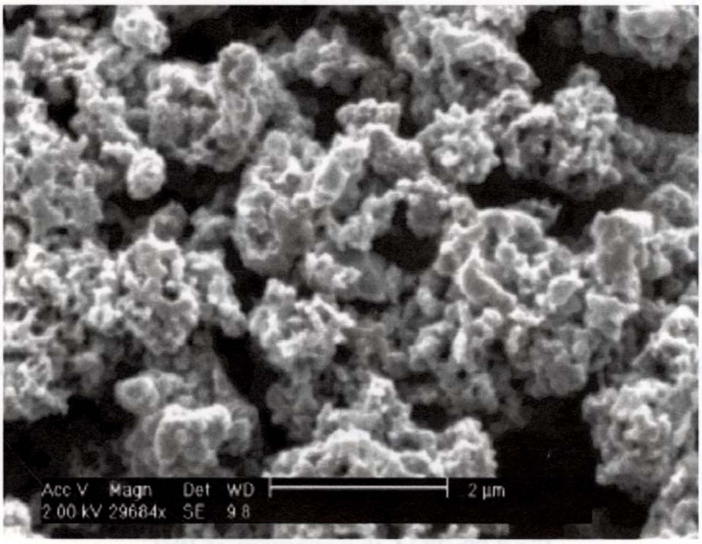


Fig.3.39: Scanning electron micrograph of polyaniline.

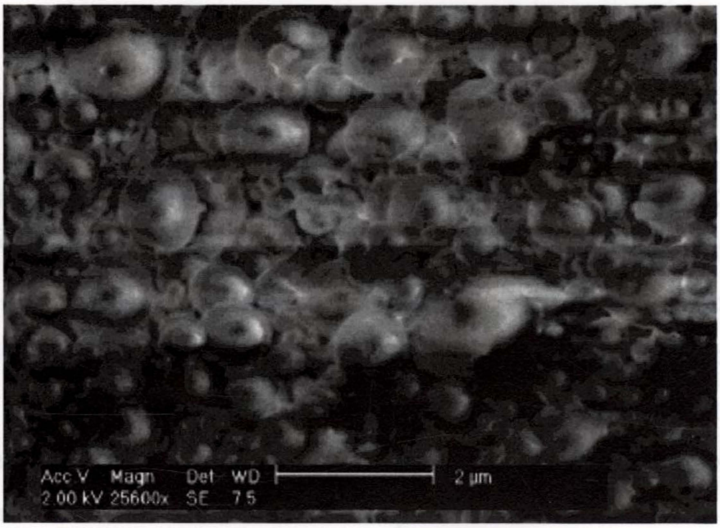


Fig.3.40: Scanning electron micrograph of PVC

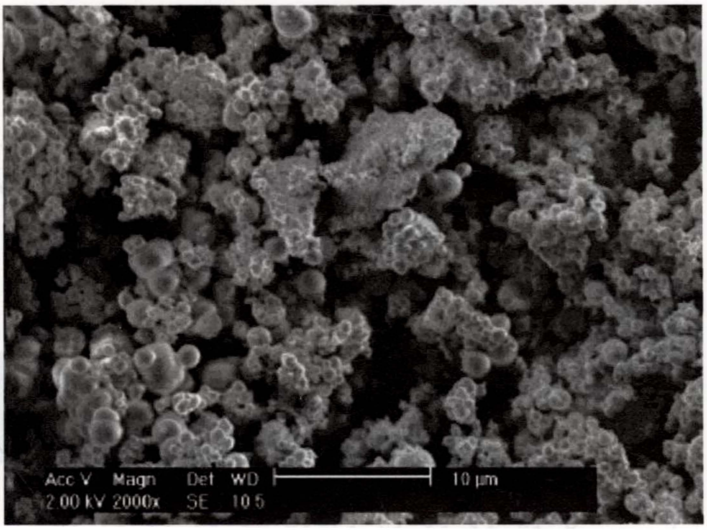


Fig.3.41: Scanning electron micrograph of Pani:PVC(1:1.5)SIPN.

3.3.1.4. CONDUCTIVITY AT LOW FREQUENCIES

Figure 3.42 shows the variation of conductivity with frequency of polyaniline and Pani: PVC SIPN of 1:1.5 composition in the frequency range from 10 Hz to 10 MHz. It is clear from the figure that the conductivity increase with increase in frequency and the effect is higher for polyaniline alone. Also a threshold frequency of 1 MHz is observed in the case of polyaniline alone but in the case of Pani: PVC SIPN the conductivity gradually increases.

Figure 3.43 shows the conductivity of polyaniline and Pani: PVC SIPN at various frequencies. The figure shows that the conductivity of polyaniline at very low frequencies is higher when compared to that of SIPN.

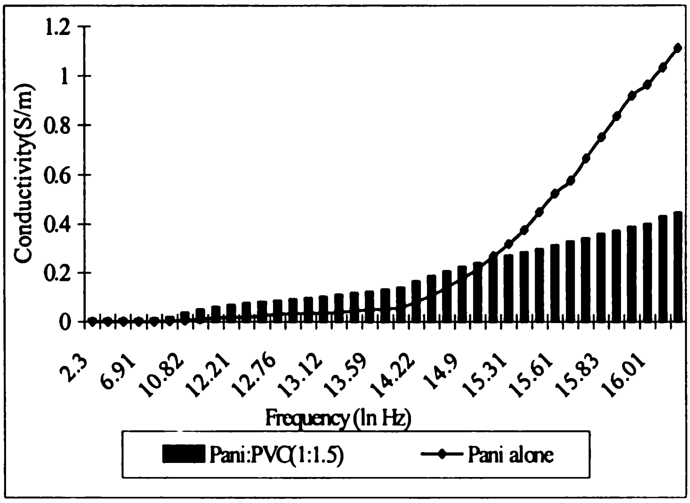


Fig. 3.42: Variation of conductivity at lower frequencies.

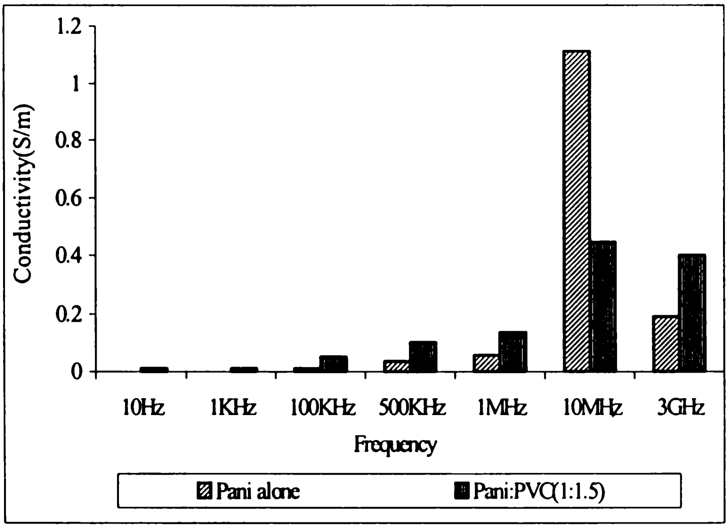


Fig.3.43: Variation of conductivity at varying frequencies.

3.3.2 Studies on Cyclohexanone Soluble Polyaniline-Polyvinyl Chloride Semi Interpenetrating Networks

The most prominent drawback of polyaniline is its processing difficulty. To overcome that difficulty conductive semi inter penetrating polymer networks based on polyvinyl chloride in powder and pellet forms are prepared and its dielectric properties are studied in part II. But the main drawback of powder form is its non uniformity in a solvent. To overcome this drawback, a solvent soluble Pani:PVC SIPN is prepared and its dielectric properties are studied in this section. Cyclohexanone solvent is used for the study.

3.3.2.1. EXPERIMENTAL

- ***Materials Used***

1.Aniline (reagent grade) is distilled prior to use.

2.Ammonium per sulphate, emulsion grade Polyvinyl chloride and cyclohexanone were used as received.

- ***Preparation of Polyaniline-Poly vinyl chloride SIPN in film form***

Chemical oxidative polymerization of aniline is carried out using ammonium per sulphate as initiator in the presence of emulsion grade polyvinyl chloride solution in cyclohexanone. The polymerization is carried out for about 4 hrs. at room temperature. It is then made in to film by solution casting and is doped with 1M HCl. The dielectric properties and conductivity of these SIPN's are measured using cavity perturbation technique. Different compositions of PAN-PVC SIPN's, say, 1:0.5, 1:1, 1:1.5,1:2 are prepared using the above procedure. Studies are conducted in S, C and X bands of microwave frequencies.

3.3.2.2. RESULTS AND DISCUSSION

(a) Variation of dielectric properties with frequency

1. Dielectric loss, Conductivity and loss tangent.

Fig. 3.44 shows the variation of the dielectric loss of different SIPN's in film form, from 2 GHz to 12 GHz.

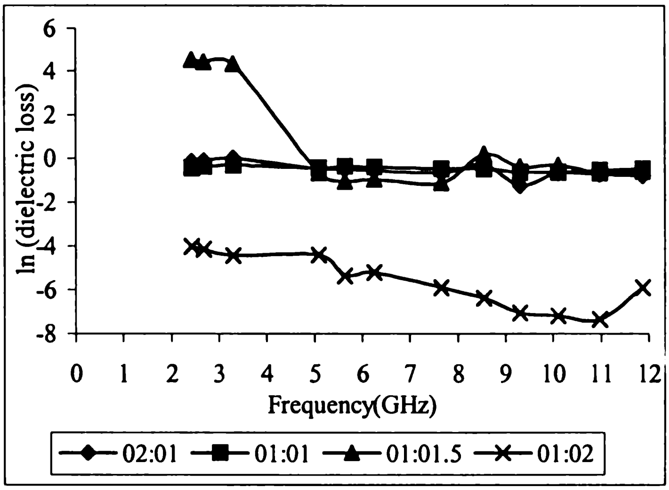


Fig 3.44: variation of dielectric loss with frequency.

The dielectric loss is found to be high at lower frequency, i.e., in the S band especially in the case of 1:1.5 composition. The dielectric loss is a direct function of relaxation process and the origin of this relaxation is due to the local motion of polar groups. The dielectric loss is very high at low frequencies due to the free charge motion within the material. There is time for charges to build up at the interfaces before the field changes the direction and this contributes to the high dielectric loss at lower frequencies.

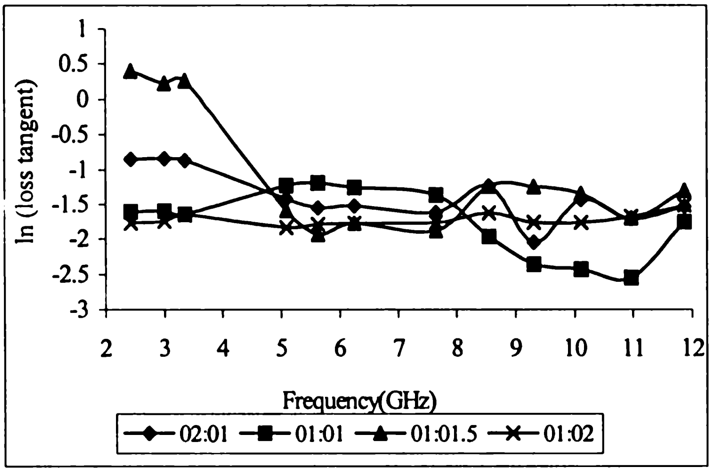


Fig 3.45 : Variation of loss tangent with frequency.

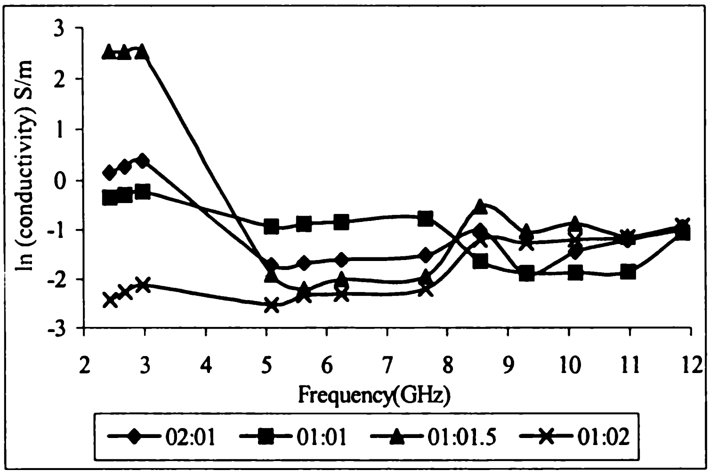


Fig 3.46: Variation of conductivity with frequency.

Figure 3.45 shows that the loss tangent (tanδ) is directly related to the dielectric loss factor. Fig.3.46 shows the conductivity of different SIPN's with frequency. It shows the same behaviour as the dielectric loss factor.

2. Dielectric constant (ε'_r)

Fig 3.47 shows that the dielectric constant decreases with increase in frequency. It is due to the orientation polarization as explained earlier. At higher frequencies rotational displacement of molecular dipoles under the influence of alternating field may lead to dielectric relaxation and this leads to a decrease in dielectric constant[62].

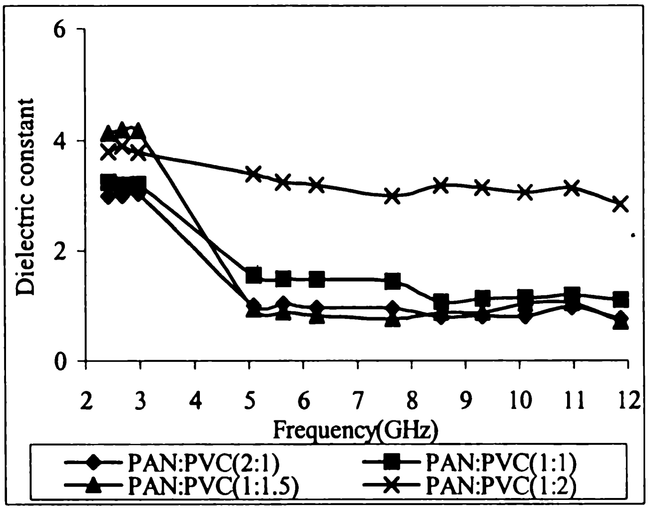


Fig 3.47: variation of dielectric constant with frequency.

Figure 3.48 shows the variation of dielectric heating coefficient of different SIPN's with frequency. It is observed from the figure that the SIPN's show very good dielectric heating property, along the S band ie, the dielectric heating coefficient is minimum.

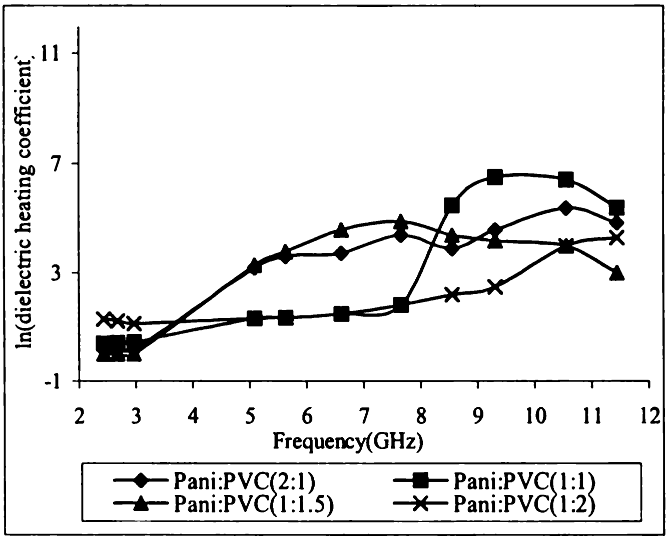


Fig 3.48 : Variation of dielectric heating coefficient with frequency.

(b) Variation of dielectric properties of SIPN's with compostions

Figures 3.49, 3.50 and 3.51 show the variation of conductivity, dielectric constant and dielectric heating coefficient of different proportions of Pani:PVC SIPN's in S, C, and X bands respectively.

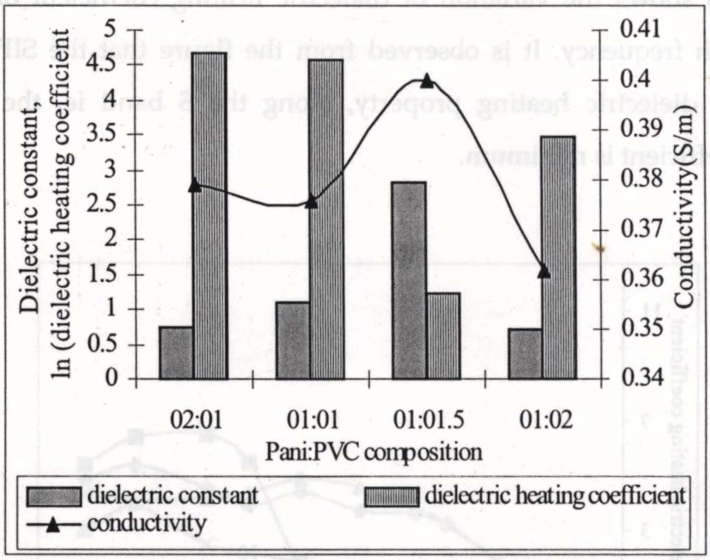


Figure 3.49 : Variation of dielectric properties at S band(2.97 GHz).

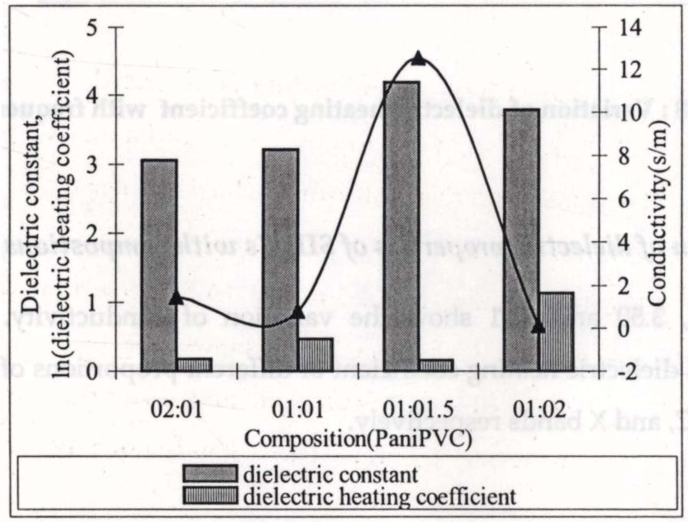


Figure 3.50: Variation of dielectric properties at C band(7.64 GHz).

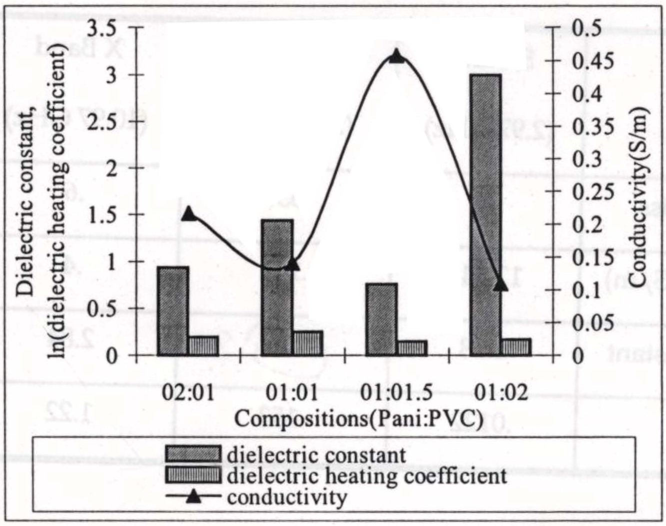


Figure 3.51: Variation of dielectric properties at X band (10.97 GHz)

It is clear from the figure that the conductivity is increased with increase in PVC content and it reaches a maximum at 1:1.5 Pani:PVC proportion, irrespective of the bands. The reason for this behaviour is same as explained earlier. Table 3.4 shows the variation of conductivity, dielectric loss, dielectric constant and dielectric heating coefficient for 1:1.5 proportion at different bands. It is clear from the table that the S band shows very high dielectric loss, high conductivity, high dielectric constant and low dielectric heating coefficient compared to C and X bands. The X band shows better properties compared to C band.

Table 3.4: Dielectric properties of 1:1.5 SIPN at S, C, X bands.

	S Band (2.97 GHz)	C Band (7.56 GHz)	X Band (10.97 GHz)
Dielectric loss	76	.331	.6
Conductivity(S/m)	12.549	.141	.4
Dielectric constant	4.18	.76	2.84
ln J	.0122	.153	1.22

The high conductivity at ISM (Industrial, Scientific and Medical) frequencies are beneficial for commercial applications. Table 3.5 shows that the absorption coefficient is very high for 1:1.5 proportion and the skin depth is very low.

Table 3.5: Absorption coefficient and skin depth of Pani:PVC SIPN at S band at 2.97 GHz.

Property	Composition(Pani:PVC)			
	2:1	1:1	1:1.5	1:2
Absorption coefficient(m^{-1})	29.9	57.6	235	30
Skin depth(m)	0.03	0.02	0.004	0.031

3.3.3. Comparison of Powder, Pellet and Film Forms of SIPN

(a) Comparison of dielectric properties

The important dielectric properties like dielectric loss, conductivity, dielectric constant and dielectric heating coefficient of 1:1.5 proportions of Pani :PVC SIPN's are compared in table 3.6. It is clear from the table that the dielectric loss and conductivity is higher for film samples compared to powder which inturn is higher compared to pellet samples. The higher dilution of the matrix in film form compared to powder form increases the conductivity. The film samples shows minimum heating coefficient compared to powder and pellet samples.

Table 3.6: Comparison of powder, pellet and film samples of 1:1.5 Pani:PVC SIPN at 2.97 GHz.

	Powder	Pellet	Film
Dielectric loss	27	2.13	76
Conductivity(S/m)	4.06	.35	12.549
Dielectric constant	14	9.6	4.18
Loss tangent	1.9	0.22	4.3
In J	0.026	0.995	0.0122

Table 3.7 shows the absorption coefficient and skin depth of powder, pellet and film samples at 1:1.5 composition. It is clear from the table that the absorption coefficient is high and skin depth is low for film sample. The skin depth is very near to zero for the film sample and it is very useful in microwave applications.

Table 3.7: Absorption coefficient and skin depth of powder, pellet and film form of Pani: PVC SIPN's at 2.97 GHz

Property	Powder	Pellet	Film
Absorption coefficient(m^{-1})	91	21	235
Skin depth(m)	0.01	0.05	0.004

(b) Comparison of TGA and DSC studies

- **TGA studies**

Figure 3.52 shows the thermograms of powder and film form of optimized proportion of Pani: PVC(1:1.5) SIPN. The initial loss between 100-280°C in both sample is due to the evolution of dopant molecules. In the case of powder samples a weight loss of 50 % is observed due to the degradation of PVC and polyaniline chain at a temperature between 280-400°C. Further degradation of polyaniline taking place after 400°C. But in the case of film samples the degradation of polyaniline and polyvinyl chloride shows a continuous loss from 250°C. This indicates that the effect of PVC on polyaniline is much greater when compared to powder samples.

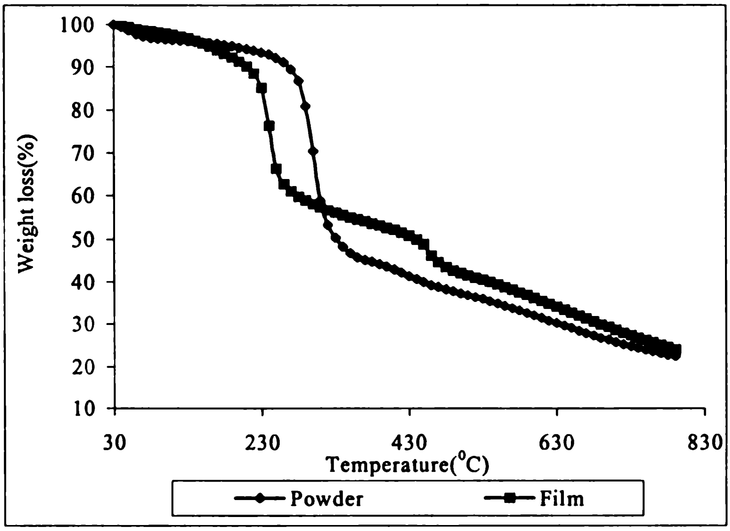


Fig.3.52: TGA thermogram of powder and film form of

1:1.5 (Pani:PVC) SIPN.

◆ ***DSC studies***

Figure 3. 53 shows that the glass transition temperature (Tg) of PVC is shifted to 67°C and the Tg of polyaniline (128°C) is shifted to 125°C in powder sample. In the case of film form the Tg of polyaniline is futher shifted to lower value, i.e., to 100°C. The lower Tg shift of Pani in the SIPN's shows that the PVC act as a plasticiser in polyaniline. The lower Tg vlaue of film sample also indicates that the PVC chain is more near to the polyaniline chain compared to

the pellet sample. And therefore the polyaniline in film form is more flexible and has improved the dielectric properties at the microwave frequencies.

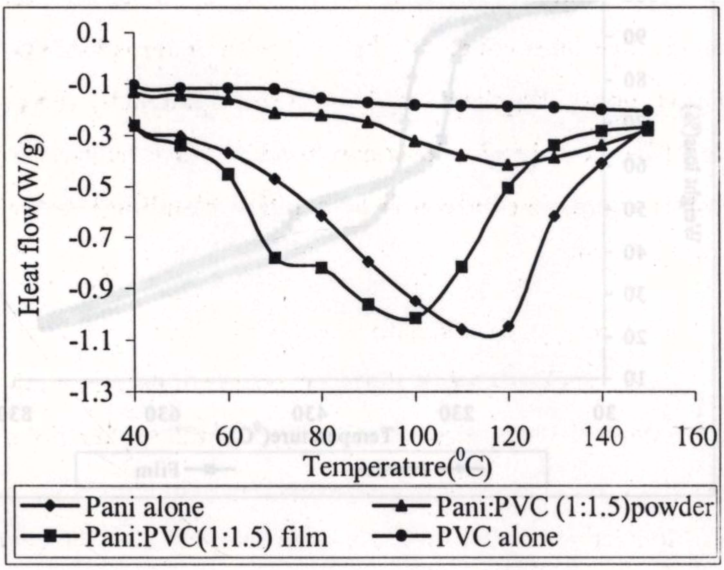


Fig.3.53: DSC thermogram of powder and film samples of 1:1.5 Pani:PVC SIPN

PART III

3.4. STUDIES ON POLYANILINE-NATURAL RUBBER COMPOSITES

3.4.1 INTRODUCTION

As far as the processability and mechanical properties are concerned, the modification of conducting polyaniline at microlevel needs to be accomplished. Incorporation of flexible elastomers into relatively rigid polyanilines through blending[63,64], in-situ polymerizations[65], or interpenetrating networks[66,67] has attracted considerable attention. Copolymers with core shell structures have also been chosen. Based on this concept, polybutadiene rubber latex covalently bonded with water-soluble polyaniline, as the shell was reported[68]. Conductivity is also imparted by the addition of finely divided fillers of high intrinsic conductivity, such as carbon black[69,70]. Also the plastics are made conducting by solution blending[71,72], dry blending or by melt processing[73] .

Among the conductive elastomers, natural rubber is the potential one for opto-electrical applications. Considering the easy pocessability, cost effectiveness and all the mechanical properties, conducting natural rubber holds a better position among all the conductive elastomers. Very few papers are reported based on conductivity of natural rubber[74]. We attempted to make a conducting natural rubber by simple compounding with polyaniline and the dielectric properties are studied in the microwave field. Also we report an in-situ polymerization to make conductive natural rubber latex.

3.4.2 *Studies on Natural Rubber Compounded with Polyaniline*

3.4.2.1 EXPERIMENTAL

- **Materials**

ISNR-5, Compounding ingredients, poly aniline etc.

- **Preparation**

The compounds as per the formulation (table 3.8) is mixed in a two-roll mill size (15 x 33 cm) and the compounds are kept for 24 hrs for maturation. The optimum cure time at 150°C is determined using Goettfert Elastograph model 67.85. The compounds are compression moulded at 150°C, in an electrically heated hydraulic press, into 1mm thick sheets. For this, the mould is preheated to 150°C, a piece of preformed material is placed directly in the mould cavity and compressed under a hydraulic clamp pressure of 200 kg cm^{-2}. Upon completion of the required cure cycle, the pressure is released and the sheet is stripped from the mould and suddenly cooled by plunging into cold water. After a few seconds the sample is taken from water and is dried. When the amount of polyaniline is increased it is very difficult to compound due to stickiness. Hence the amount of polyaniline is limited to 15 phr. The sheets are cut into rectangular shape to measure the dielectric properties in the microwave frequencies.

Table 3.8: Formulation

MIX	A0	A1	A2	A3
Natural rubber	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Butyl xanthate	1	1	1	1
ZDC	.75	.75	.75	.75
Sulphur	2.5	2.5	2.5	2.5
Polyaniline	0	5	10	15

3.4.2.2 RESULTS AND DISCUSSION

(a) Variation of dielectric properties with frequency

Figure 3.54 and 3.55 shows the variation of dielectric loss and conductivity of samples with frequency respectively. It is clear from the figures that the influence of frequency on the dielectric loss and conductivity is less because of the low polarity of the medium. The figures also show that the effect of frequency is pronounced only with the A3 mix which containing a higher percentage of polyaniline.

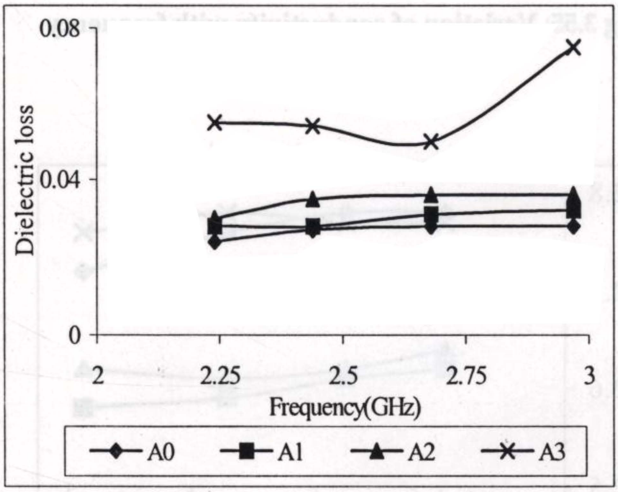


Fig 3.54:Variation of dielectric loss with frequency

The figures also show that the dielectric loss and conductivity is higher for A3 mix compared to other mixes.

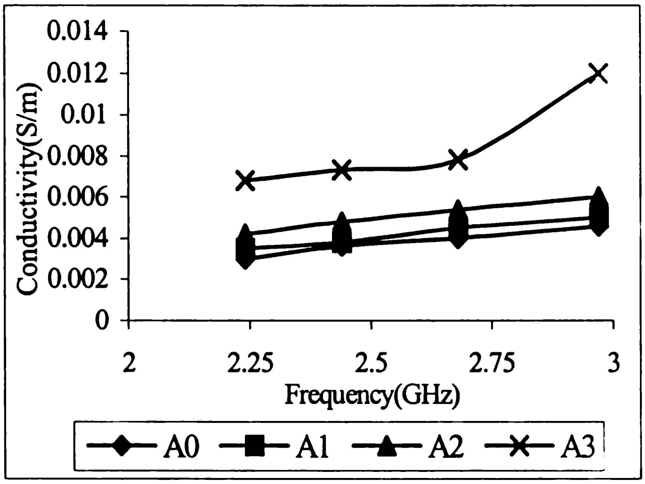


Fig 3.55: Variation of conductivity with frequency

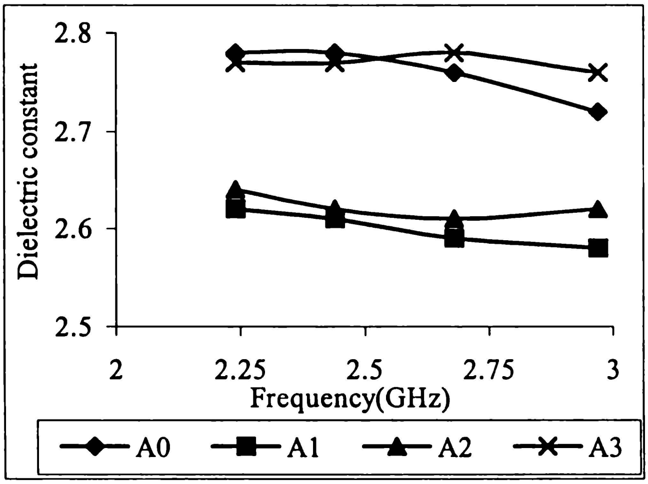


Fig 3.56: variation of dielectric constant with frequency.

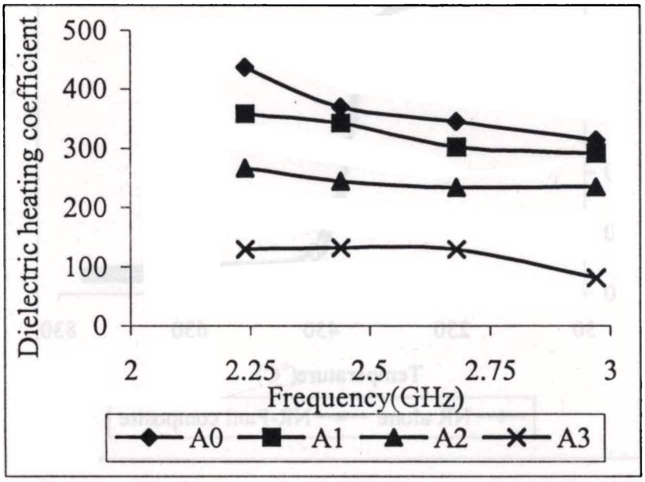


Fig 3.57: variation of dielectric heating coefficient with frequency.

Similarly figures 3.56 and 3.57 indicates that the change in frequency has little effect on the dielectric constant (3.56) and dielectric heating coefficient (3.57) except for A3 mix. The reason for the variation of dielectric properties of A3 mix with frequency is same as explained in the previous sections. The heating property of conducting NR is very poor due to the very high dielectric heating coefficient.

(b) TGA studies

Figure 3.58 shows the TGA thermogram of NR alone and that of A3 mix. In both cases the initial weight loss is observed between 100-300^{o}C. In the case of NR alone it may be due to the water evolution and in the case of SIPN it may be due to the evolution of water and dopant molecule. The second weight loss of 86 % due to the degradation of natural rubber is observed between 300-450^{o}C in NR lone is reduced to 81 % in A3 mix.. This indicates that the NR is more stabilized on compounding with polyaniline.

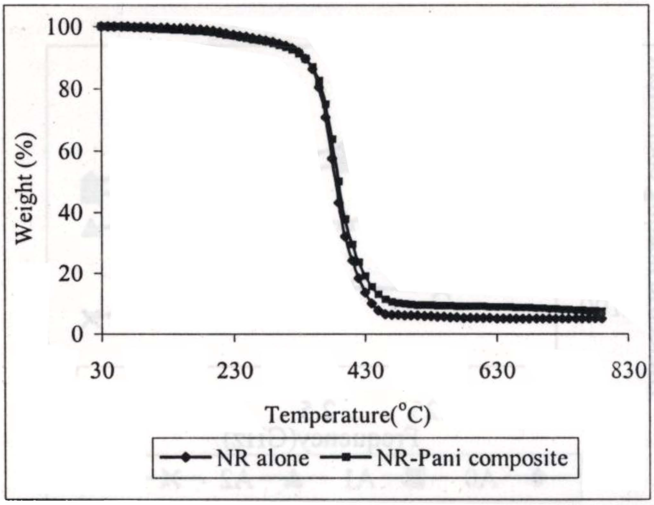


Fig.3.58: TGA thermogram of NR and NR-Pani composite.

3.4.3 Studies On Conducting Natural Rubber Latex

3.4.3.1 EXPERIMENTAL

- **Materials**

Aniline, natural rubber latex, vulkanox VL, ammonium per sulfate and 1M HCl.

- **Preparation of Polyaniline:Natural rubber(Pani:NR) SIPN**

Natural rubber latex is first stabilized with vulkanox VL and is converted to positively charged latex (positex) using HCl in order to avoid coagulation during polymerization. Also the positive latex helps in the preparation of doped Pani-NR SIPN. Aniline is added to positive latex and it is then polymerized using ammonium persulphate as the initiator. The reaction is carried out at room temperature for 4 hrs. Different proportions of Pani: NR

SIPN's, say, 2:1,1:1,1:2 are prepared and the dielectric properties are studied at the microwave frequencies.

The in-situ polymerization of aniline in the presence of positive NR latex loses its film property. Inorder to take the measurements, it is coagulated with NaOH solution. It is then doped with 1M HCl. After coagulation a uniform sheet of polyaniline - NR compound is made by passing through the tight nip of a two-roll mill.

After the coagulation Pani:NR SIPN can be dissolved in toluene and it can be made into film very easily. This phenomenon indicates that the polyaniline molecules bound the rubber particles. The polyaniline bound natural rubber latex is stable and it can be considered as a natural rubber modified water soluble polyaniline latex. Considering the stability of polyaniline latex and also the difficulty for the formation of film, the nature of SIPN can be considered as a core-shell structure. That is, polyaniline shell with natural rubber core as in pani coated polystyrene latex[75] and polybutadiene-PSS latex.

3.4.3.2 RESULTS AND DISCUSSION

(a) Dielectric properties

1. Dielectric loss and conductivity

The effect of frequency on dielectric loss and conductivity is very little as shown in the figures 3.59 and 3.60.

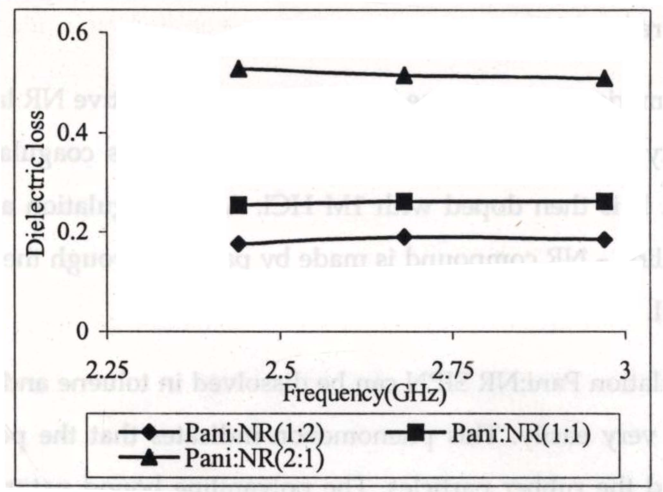


Figure 3.59: Variation of dielectric loss of Pani:NR SIPN's with frequency

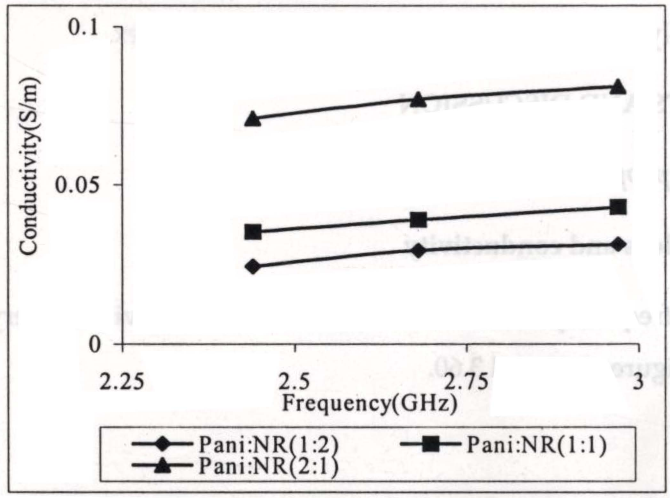


Figure 3.60 Variation of conductivity of Pani:NR SIPN's with frequency

The dielectric loss and conductivity are slightly increased with increase in frequency. It may be due to the firm contact of polyaniline molecules with the non polar NR through core-shell structure. It is also evident from the figures that the dielectric loss and conductivity are higher for 2:1 (Pani: NR) composition due to the higher percentage of polyaniline.

2. Dielectric constant

It is clear from the figure 3.61 that the dielectric constant is also less affected by the change in frequency. But there is a shift of values of dielectric constant from the normal dielectric constant of natural rubber (i.e., 2) due to the presence of polyaniline. The dielectric constant is higher for 2:1 composition.

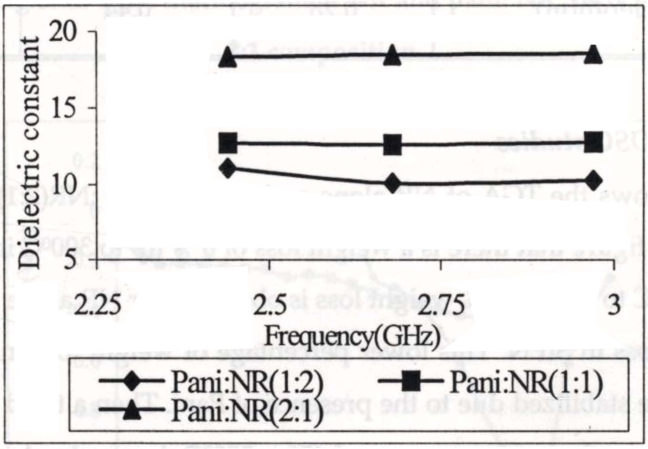


Figure 3.61 Variation of dielectric constant of Pani:NR SIPN's with frequency.

3. Absorption coefficient and skin depth

Table 3.9 shows the absorption coefficient and skin depth of different proportions of Pani:NR SIPN. It is seen from the table that the absorption coefficient is high and skin depth is low for 2:1 composition. Natural rubber will allow the passage of electromagnetic radiation and when the polyaniline content is increased the electromagnetic radiation's are restricted to penetrate.

Table 3.9: Absorption coefficient and skin depth of Pani:NR at 2.97 GHz.

Property	Composition(Pani:NR)		
	2:1	1:1	1:2
Absorption coefficient (m^{-1})	3.5	2.27	1.73
Skin depth(m)	0.28	0.44	0.58

(b) TGA and DSC studies

Figure 3.62 shows the TGA of NR alone and that of Pani :NR(2:1) SIPN. It is clear from the figure that there is a weight loss of 6 % up to 300^{0}C in both cases and from 300^{0}C to 450^{0}C 85 % weight loss is observed for NR alone is shifted to 54 % weight loss in SIPN. This lower percentage of weight loss indicates that the NR is more stabilized due to the presence of Pani. Then a third weight loss of 25 % is observed at a temperature of 450 - 550^{0}C due to the degradation of polyaniline.

Figure 3.63 shows the DSC thermogram of Pani and Pani:NR SIPN. It is clear from the figure that the Tg of NR is shifted to -65^{0}C and that of Pani is shifted to 105⁰C. The lower Tg shift of Pani is due to the presence of more flexible natural rubber.

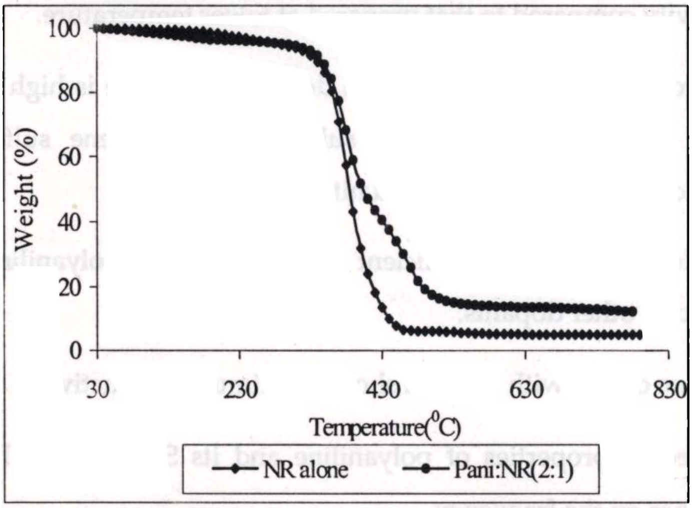


Fig.3.62: TGA thermogram of NR and pani: NR SIPN of 2:1 composition.

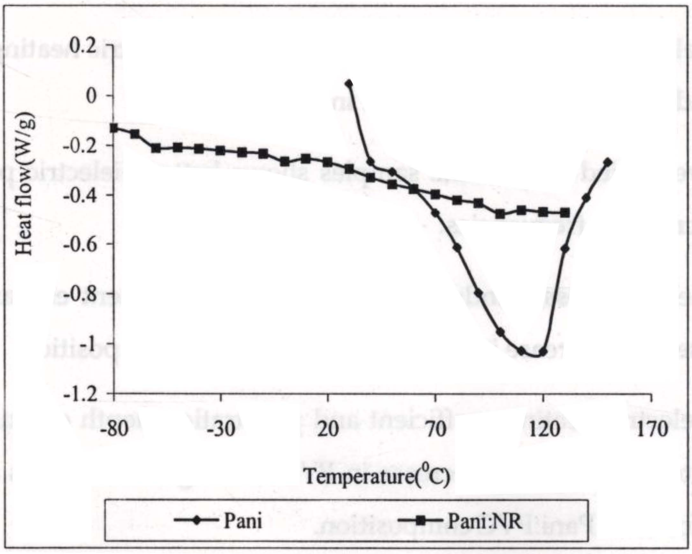


Fig.3.63: DSC thrmogram of Pani and Pani:NR SIPN.

3.5 CONCLUSIONS

- Polyaniline prepared at room temperature shows a high microwave conductivity compared to that prepared at lower temperature.
- The microwave conductivity of HCl doped polyaniline is high compared to other dopants like camphor sulfonic acid, toluene sulfonic acid, perchloric acid, sulphuric acid and nitric acid.
- The dielectric heating coefficient of HCl doped polyaniline is less compared to other dopants.
- Polyaniline doped with 1M HCl shows maximum conductivity.
- The dielectric properties of polyaniline and its SIPN's with PVC show dependence on the frequency.
- The conductivity, dielectric loss, loss tangent and absorption coefficient are found to increase with increase in frequency.
- The dielectric constant, penetration depth and dielectric heating coefficient is found to decrease with increase in frequency.
- The oven dried polyaniline samples shows better dielectric properties in the microwave frequencies.
- The dielectric loss, conductivity, absorption coefficient etc. are found to increase with increase in PVC loading up to 1:1.5 composition.
- The dielectric heating coefficient and penetration depth or skin depth are found to decrease with increase in PVC loading and it shows a minimum value for 1:1.5 Pani:PVC composition.

- The microwave conductivity and absorption coefficient of film (soluble form) samples is very high compared to powder samples which inturn higher than the pellet samples.
- The dielectric heating coefficient and the penetration depth are less for film samples.
- The processing difficulty of polyaniline is overcome by preparing conducting soluble Pani: PVC SIPN.
- Absorption coefficient is very high, the penetration depth is very low, for the soluble SIPN (film) of 1:1.5 and this composition can be used for EMI shielding applications.
- Pani :NR SIPN can be successfully prepared by the in-situ polymerization technique.
- Pani :NR SIPN of 2:1 composition gives better dielectric properties.

3.6: REFERENCES

1. H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang and A.J. Heeger, *J.Chem.Soc.,Chem. Commun.*, 578, (1977).
2. N. Li. Lee and L. H. Ong., *J.Appl.Electrochem.* 22,512, (1992).
3. F.Trinidal, M.C. Montemayer and E. Falas., *J. Electro chem. Society* 138,3186, (1991).
4. Y.Cao, P.Smith and A.J. Heeger, *Synth.Met.*, 48,91(1992).
5. N.Kuramato,Jeff C. Michaelson, A.J.McEvoy and M.Gratzel., *J.Chem.Commun*, 1478-1480(1990).
6. N.Kuramato., *J. Pn.Kokai Tokkyo Koho,JP 06,*279,584(1993).
7. E.M. Genies, A.Boyle, M.Lapkowski, C.Tsintavis, *Synth.Met.* 36,139,1990.
8. J.P.Travers, F.Genoud, C.Menardo and M.Nechtschein, *Synth.Met.* 35,159(1990).
9. A.G.MacDiarmid, A.J.Epstein, *J.Chem. Soc., Faraday Discuss.*, 88,317(1989).
10. F.Lux, *Polymer*, 35,2915(1994).
11. A.G.macDiarmid, *Conjugated polymers and relaxed materials,* proc.81st Nobel Symp., Lulea,Sweden,(1991),Oxford Univ. Press, Oxford,(1993).
12. J.R.Reynolds, M. Pomerantz, Electro responsive molecular and polymeric systems, marcel Dekker, new York, p.187 (1991).
13. T.Matsunaga, H.Daifuka, T.Nakajima,T.Kawagoe., *Poly.Adv Technol* 1,33(1990).
14. J.C.Lacroix, K.K.Kanazawa, A.Diaz, *J.Electrochem Soc* 136,1308(1989).
15. M.Morita, *J.Polym Sci B Polym Phys* 32,231(1994).

16. G.Gustafsson, Y.Cao, G.M.Treacy, F.Klavetter, N.Colaneri, A.J.Heeger, 357,477(1992).

17. R.H.Baughman, *Synth Met* 78,339(1996).

18. S.A.Chen, Y.Fang, *Synth Met* 60,215(1993).

19. F.Wudl, R.O. Angus, F. L. Lu, P.M.Allemand, D.J.Bachon, M.Novak, Z.X.Liu, A.J.Heeger, *J.Am Chem Soc* 109,3677(1987).

20. G.Yu, A.J.Heeger, *Synth Met* 85,1183(1997).

21. K.L.Nagai and R.W Rendell, *'Handbook of conducting* polymers' 1986, (Ed.T.A.Skotheiim).Marcel Dekker, New York.

22. A.Feldblum, Y.W Park,. A.J.Heeger, A.G. MacDiarimid, G. Wnek, F. Karasz,and J.C.W. Chien., *J.Poiym.Sci.:Polym. Phys.*Edn.,19,173,(1981).

23. G.Phillips, R.Suresh, J.waldman, J.Kumar, J.I.Chen, S.Tripathy and J.C. Huang, *J.Appl.Phys.*,69,899(1991).

24. J.Unsworth, A.Kaynak, B.A. Lunn, and G.E. Beard, *J. Mater. Sci.*,28,3307(1993).

25. L.J. Buckley, and K.E. Dudeck, *Synth. Met.*,52,353(1992).

26. H.H.S.Javadi, K.R. Cromack, A.G. MacDiarmid, and A.J.Epstein, *Phys.Rev. (B)*,39,3579(1989).

27. A.G. MacDiarmid, J.C.Chiang, A.F.Richter, N.L.D. Somasiri and A.J.Epestein, Polyanilines:Synthesis and charactreization of the emeraldine oxidation state by elemental analysis, in L. Alacacer(editor), Conducting polymers Dordrecht,(1987).

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

29. L.Olmedo, P.Hourquebie and F.Jousse, *Hand book of organic conductive molecules and polymers*, Vol.3, Chapter 8, Edited by H.S.Nalwa, John Wiley(1997).
30. J.G. Kirkwood and R.M.Fuoss, *J.chem. phys.*, 9,329,(1941).
31. P.Hourquebie and L.Olmedo, *Synth.Met.*, **65**, 19, (1995).
32. C.Ku. Chen, and Raimond Liepins, Electrical properties of polymers, Hanser publications, New York (1987).
33. N.G.McCrum,B.Ee. Read, G.Williams,Anelastic Dielectric Effectsb in Polymer solids, John Wiley & Sons Ltd., London,(1967).
34. R.J.Maccallum, C.A. Vincent, Polymer Electrolyte Reviews II, Elsevier Applied Science Publuishers Ltd, London and New York, (1987),Ch.2.
35. A.Kyritsis, P.Pissis, J.Grammatikakis, *J.Polym.Sci. Part B: Polym.Phys.* **33**, 1737-1750, (1995).
36. 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).
37. V.Saravanan, S. Palaniappan,S. Seetharamu, *Macromolecules New Frontiers*, **1**, 344, (1995).
38. Jayashree Anand, Palle Swapna Rao, S. Palaniappan and D. N. Sathyanarayana, *Macromolecules New Frontiers*, **1**, 374, (1998).
39. T.A Ezquerra, F.Kremmer, G.Wegner, AC, *Dielectric properties of heterogeneous Materials: Progress in Eelectromagnetic research*, vol. **6**, Elsvier, new York,(1992).
40. Bradford, I. S., Carpentier, M-H., "*The Microwave Engineering hand book*" Chapman and Hall, London, (1993).

41. Stephen, C. W., Frederic, H. L., *"Microwaves made simple: priciples and applications"* United States Bookcrafters, Chelsea, (1985).

42. John Honey,S.Bijukumar,K.T.Mathew and Joseph Rani, *J.Appl.Polym.Sci.*, **83**, 2008-2012,(2002).

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

44. S .S. Im and S. W. Byun, *J . Appl. Poly. Sci.*, **51**, 1221,(1994).

45. H. S. O. Chan, H. Hopok, E. Khor.and M. M. Tan., *Synth.Met.*, **31**, 95, (1995).

46. M. A. De Paoli, R.J.Waltman, A. F. Diaz and J. Bargon, J. Chem. Soc., Chem.commun., **1015**,(1984).

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

48. B.Tieke and W. Gabriel, *Polymer*,**31**,20, (1990).

49. M. Makhlouki, M. Morsli, A.Bonnet, A. Conan, A.Pron and S. Lefrant, *J. Appl. Polym. Sci.*,**44**,443, (1992).

50. T. K. Mandal and B. M. Mandal, *Synth. Metal*, **80**,**83**, (1996).

51. P.Dutta, S.Biswas, M.Ghosh, S.K.De, S.Chatterjee, *Synth.Met.*, **122**,455-461, (2001).

52. H.C.Pant,M.K.Patra,P.Vashistha,K.Manzoor,S.R.Vardera and N.Kumar,14th annual general meeting and theme symposium on novel polymeric materials,(2003).

53. P.Banerjee and B.M.Mandal ., *Macromolecules*,**28**,3940, (1995).

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

55. A.Pron, J.E. Osterholm, P.Smith, A.J.Heeger, J.Laska and M.Zagorska., *Synth.Met.*,57,3520, (1993).
56. M.Thangarathinavelu, A.K.Tripathi, T.C. Goel and I.K.Varma, *J.Appl.Polym.Sci.*,51,1347, (1994).
57. L.W.Shacklette, C.C.Han and M.H.Luly., *Synth.Met.*,57,3532, (1993).
58. L.Terlemezyan, M.Mihailov and B.Ivanova., *Polym.Bull.*,29,283, (1992).
59. A.B.Kaiser, C.K.Subramaniam, P.W.Gilberd and B.Wessling., *Synth.Met.*,69,197,(1995).
60. J.C.Maxwell, Electricity and Magnetism, Oxford University Press, Oxford (1892).
61. R.W.Sillars, *IEE Journal*, 80,371,(1937).
62. N.G.McCrum,B.Ee. Read, G.Williams,Anelastic Dielectric Effectsb in Polymer solids, John Wiley & Sons Ltd., London, (1967).
63. G.L.Mantovani, A.G.MacDiarmid, L.H.C. Mattoso, *Synth. Met.*,84,73,(1997).
64. M.R.Vallim, M.I.Felisberti, M.A.De paoli, *J.Appli.Polym.Sci.*, 75,677,(2000).
65. J.Stejskal, I.Sapurina, J.Prokes, J.Zemek, *Synth.Met.*, 105,195,(1999).
66. L.Y.Wang, L.Y.Chiang, C.S.Kuo, J.G.Lin, C.Y.Huang, *Mater.Res.Soc.Symp.Proc.*413, 571,(1996).
67. L.Y.Chiang, L.Y.Wang, C.S.Kuo, J.G.Lin, C.Y.Huang, *Synth.Met.*84,721,(1997).
68. Kuo Changshu, Y.Chiang, Kumar Jayant, K.Tripathy, *Polymer*, 41(2),1768,(2000).
69. A.I.Medalia, *Rubber Chem.Technol.* 59,432,(1986).
70. M.H.Poleey and B.B.Boonstra, *Rubber Chem.Technol.*, 30,170,(1957).

71. M.Angelopoulos,N.Patel, and R.Saraf, *Synth.Met.*, 55,1552,(1993).

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

73. L.W.Shacklette, C.C.Han, and M.H.Luly, *Synth.Met.*, 57,3532,(1993).

74. R.Sreeja, P.Pradeep and Alex Rosamma, *15th Kerala sci. cong.Proc.*(2003).

75. C.Barthet, S.P.Armes, S.F.Lascelles, S.Y.Luk, H.M.E.Stanley, *Langmuir*, **14**,2032,(1998).

Chapter 4

STUDIES ON POLY o-TOLUIDINE AND ITS COMPOSITES

4.1. INTRODUCTION

Polyaniline (Pani) is reported to be the first conducting polymer synthesised[1] and Pani was described as existing in four different oxidation states[2-5] each of which is an octamer. The main disadvantages of polyaniline are its insolubility in common organic solvents and infusibility. Incorporation of polar functional groups or long and flexible alkyl chains in the polymer backbone is a common technique to prepare Pani-type soluble polymer. For example poly o-toluidine or methyl substituted polyaniline are more soluble than the unsubstituted polyanilines.

Among the large variety of conducting polymers, polyaniline and its derivatives have received much attention because of its various technological applications[6,7], reversible proton doping, high electrical conductivity and ease of bulk preparation[8]. Green and Woodhead[2] achieved the first chemical synthesis of poly o-toluidine (PoT) as an analogue of polyaniline in 1910. Poly o-toluidine is generally prepared by the direct oxidation of toluidine using appropriate chemical oxidants or by electrochemical means using different electrode materials[9,10]. The synthetic strategies and reaction mechanisms for poly o-toluidine are similar to those of polyaniline.

Leclerc et al[11,12], have observed that the polymerisation yield is strongly influenced by the bulkiness and position of the substituent. Since an ortho position is blocked in PoT, relatively fewer ortho couplings can be expected, leading to a more regular head to tail polymer structure and thereby higher polymerisation yields. Moreover, higher molecular weights can be obtained by chemical synthesis than by electro chemical synthesis.

The conductivity of poly o-toluidine is lower by two to three orders of magnitude compared to that of Pani. The conductivity of poly o-toluidine base is less than 10^{-10} S/cm, which indicates that the acid part has been expelled from the polymer chain. The conductivity of poly o-toluidine when it is doped with different dopants like HCl, HNO_3, H_2SO_4, I_2, $HClO_4$ were reported[13,14]. The decrease in conductivity in PoT can be attributed to their electronic structure. The observation of pauli paramagnetism in polyo-toluidine[13,14] reveals the existence of a degenerate electronic structure with a finite density of states at the fermi energy as in Pani[15]. MacDiarmid et al[16-18] studied the electron localization in poly o-toluidine which leads to a reduced conductivity. It has been studied in depth for d.c and microwave conductivity's, dielectric constant, a.c. conductivity and thermopower measurements. Wang et al[19] have inferred from the much smaller d.c conductivity, microwave conductivity and dielectric constant of PoT-HCl salt at 6.5 GHz compared to that of polyaniline-emeraldine salt[20], that the

PoT-ES system is more localized. The PoT-HCl salt has the same electronic structure as Pani-HCl, but it shows a significantly decreased conductivity[21]. The origin of this divergent result is stated to be due to increased localization of conduction electrons in POT as compared to Pani. And it is caused by the reduction in interchain interactions due to increased inter chain separation[22]. To improve the solubility and hence the solution processing for various applications poly o-toluidine is envisaged. The introduction of a substituent group (-CH_3 group in *o*-toluidine) would increases the torsion angle between the two adjacent phenylene rings and facilitates better solvation at the -NH group on the polymer back bone[23].

In this chapter we report the synthesis, characterization, and study of dielectric properties of poly o-toluidine at microwave frequencies. Also a report of the synthesis and dielectric properties of a copolymer of o-toluidine with aniline and poly o-toluidine-polyvinyl chloride semi interpenetrating networks (PoT/PVC SIPN) is given.

PART 1

4.2. STUDIES ON POLY o-TOLUIDINE AND ITS COPOLYMER

4.2.1. Studies On Poly o-Toluidine

- ***Materials Used***

1. o-toluidine, (reagent grade) is distilled prior to use.
2. Ammonium per sulphate, HCl (analar grade).

◆ *Preparation*

Chemical oxidative polymerisation of *o*-toluidine[14] is carried out using ammonium per sulphate as the initiator in the presence of 1M HCl. The polymerisation is carried out for about 4 hrs. at room temperature. It is then filtered washed and dried under different conditions like room temperature (48 hrs.), in oven (at 50 °C for 6hrs.), in vacuum (at room temperature, for 16 hrs.). The dielectric properties of these samples are measured using cavity perturbation technique.

4.2.1.1 RESULTS AND DISCUSSION

(a) Effect of drying condition on the conductivity

Figure 4.1 shows the variation of conductivity of differently dried poly o-toluidine with frequency. It is clear from the figure that the conductivity is higher for oven dried sample as in the case of polyaniline.

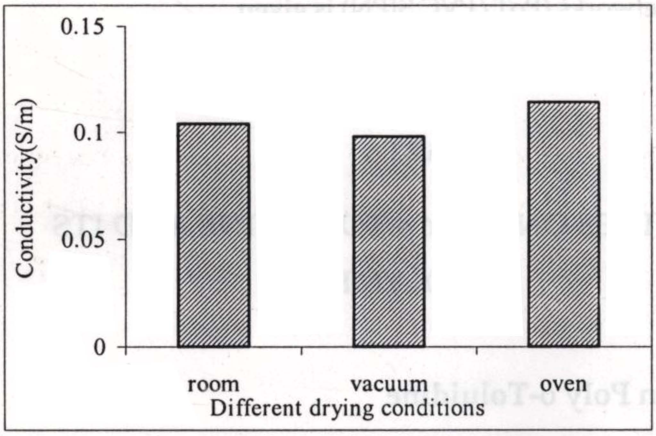
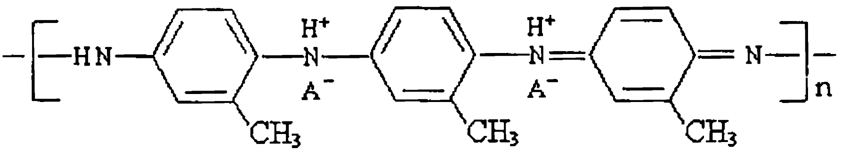


Fig.4.1: Effect of drying on conductivity at 2.97 GHz.

Protonation in PoT leads to the formation of radical cations by an internal redox reaction which causes reorganization of electronic structure to give semiquinone radical cations. The degree of protonation and the electronic conductivity thus become a function of dopant concentration as in polyaniline.



STRUCTURE OF CONDUCTING POLYO-TOLUIDINE

It is evident from the experiment that there is a loss of dopant molecules under vacuum and room temperature drying; which reduces the dielectric loss and conductivity[26].

(b) Variation of dielectric properties with frequency

1. Dielectric loss and conductivity

Fig. 4.2 shows the variation of the dielectric loss and conductivity of oven dried PoT in pellet form with frequency. The dielectric loss and conductivity are increasing with increase in frequency. At low frequencies the dipoles synchronized their orientation with the field. But as the frequency increases, the inertia of the molecule and the binding forces become dominant and it is the basis for high dielectric loss[27].

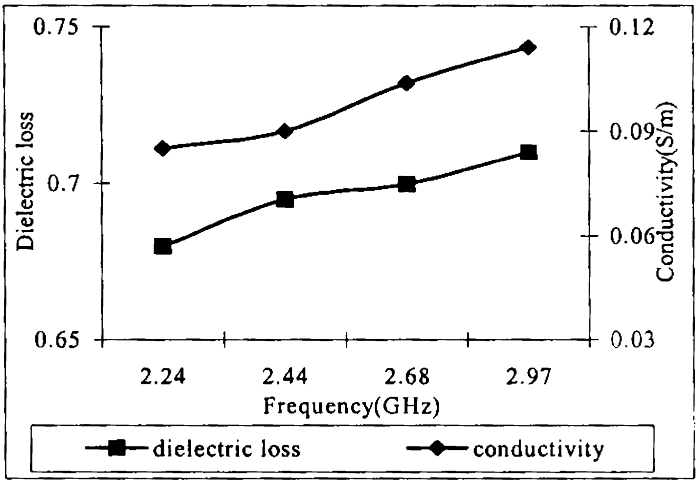


Fig.4.2 : Variation of dielectric loss and conductivity with frequency.

The microwave conductivity is directly related to the dielectric loss factor and therefore the conductivity also increases with increase in frequency as shown in the figure (4.2).

2. Dielectric constant

Figure 4.3 shows the variation of dielectric constant (real part of complex permittivity) and dielectric heating coefficient (J) with frequency. The dielectric heating coefficient and dielectric constant are decreasing with increase in frequency. Due to the polarization of dielectric materials the accumulation of charges at the inter phase between different phases of the material takes place which results in dielectric constant[22]. When the frequency is increased the orientation polarization of molecule due to the rotational displacement of polar groups reduces the dielectric constant.

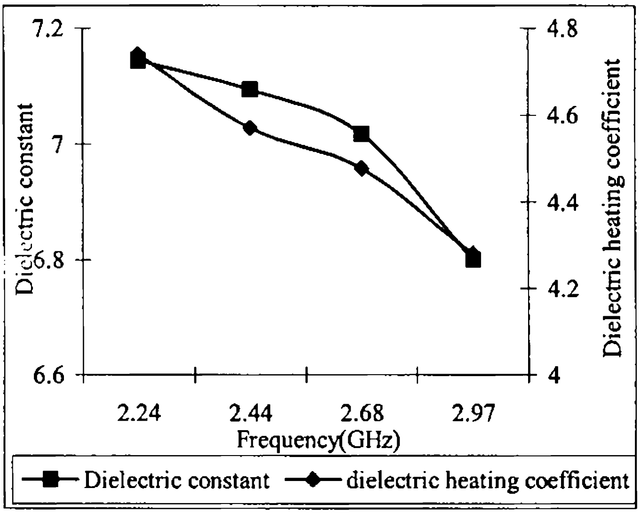


Fig.4.3: Variation of dielectric constant and heating coefficient (J) with frequency.

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

3. Loss tangent

Figure 4.4 shows the variation of loss tangent with frequency. The loss tangent increases with increase in frequency. It shows the same behaviour as that of dielectric loss factor.

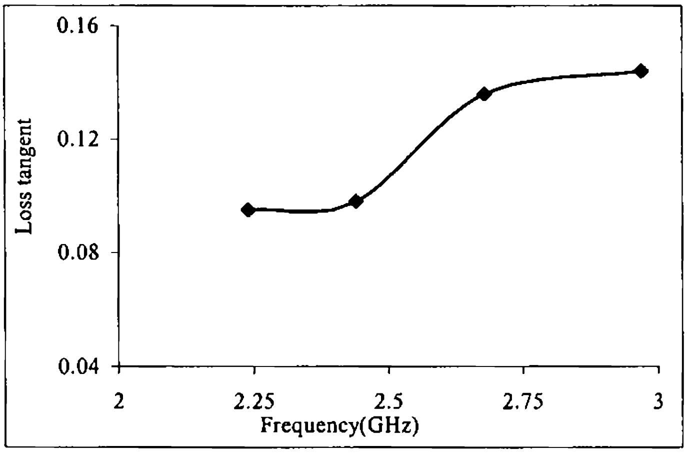


Fig. 4.4: Variation of loss tangent with frequency.

4. Absorption coefficient and skin depth

Plot of absorption coefficient of poly o-toluidine with frequency is given in figure 4.5. The absorption coefficient is directly related to the dielectric loss factor and therefore it shows the same behaviour as that of dielectric loss i.e., the absorption coefficient increases with increase in frequency.

The skin depth decreases with increase in frequency as shown in figure 4.6. The reason for this behaviour is same as explained in the case of polyaniline.

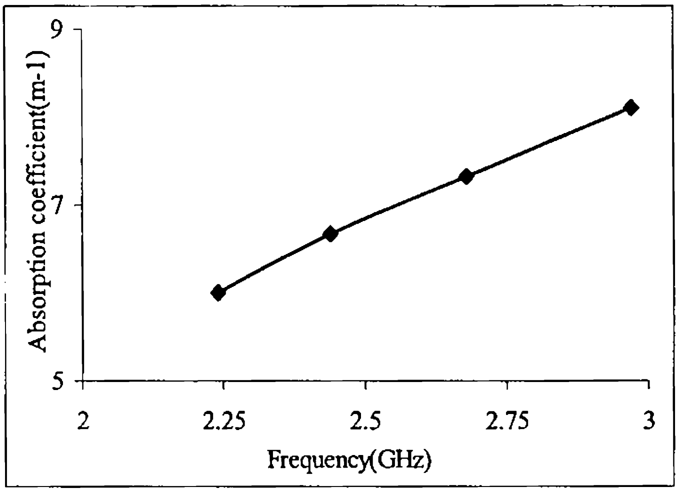


Fig 4.5: Variation of absorption coefficient with frequency.

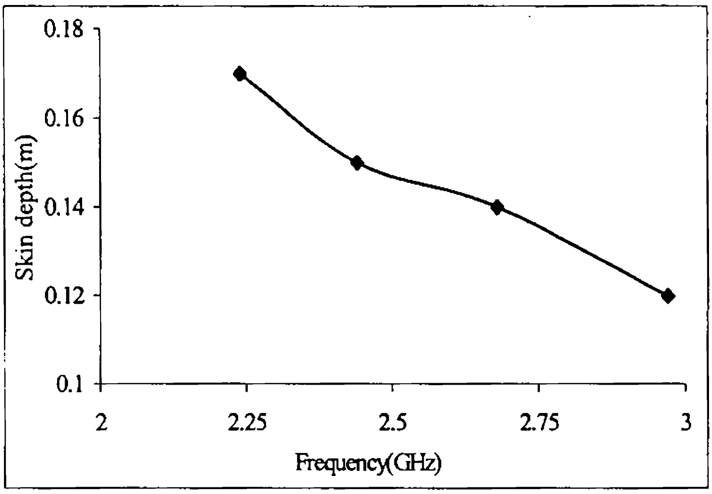


Fig 4.6: Variation of skin depth with frequency.

4.2.2. Studies On Poly (O-Toluidine Co Aniline)

To improve the processability of conducting polymers copolymerization may be a simple and convenient method. The d.c conductivity of poly (aniline *co o*-anisidine)[28,], poly (aniline-*co*-toluidine)[29,30] poly(aniline-*co*-N-butylaniline)[31,32] copolymers investigated earlier yielded fruitful results. In this section we studied the dielectric properties of poly (o-toluidine co aniline) at the microwave frequencies.

4.2.2.1. EXPERIMENTAL

◆ **Materials**

1. Aniline, *o*-toluidine (reagent grade) are distilled prior to use.
2. HCl, ammonium per sulfate are used as received.

◆ **Preparation of poly (o -toluidine co aniline)**

The copolymer is prepared by the chemical oxidative polymerization of equal proportions of aniline & *o*-toluidine carried out using ammonium per sulphate as initiator in the presence of 1M HCl. The reaction conditions are same as in the case of poly o-toluidine.

4.2.2.2. RESULTS AND DISCUSSION

(a) Characterization

Figure 4.7, 4.8 and 4.9 shows the IR spectra of polyaniline, poly o-toluidine and poly (o-toluidine co aniline). The IR spectra of polyaniline and poly o-toluidine are almost similar. The characteristic peaks of polyaniline and poly o-toluidine at 1305 cm^{-1}, due to C-H deformation, 1495 cm^{-1} and 1560 cm^{-1} due to the ring stretching modes of the quinoid and benzenoid rings are similar in the copolymer also.

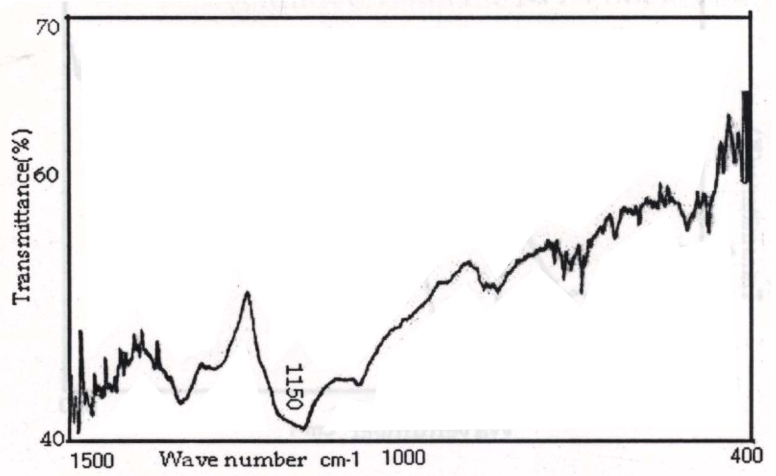


Fig. 4.7: IR spectrum of polyaniline alone.

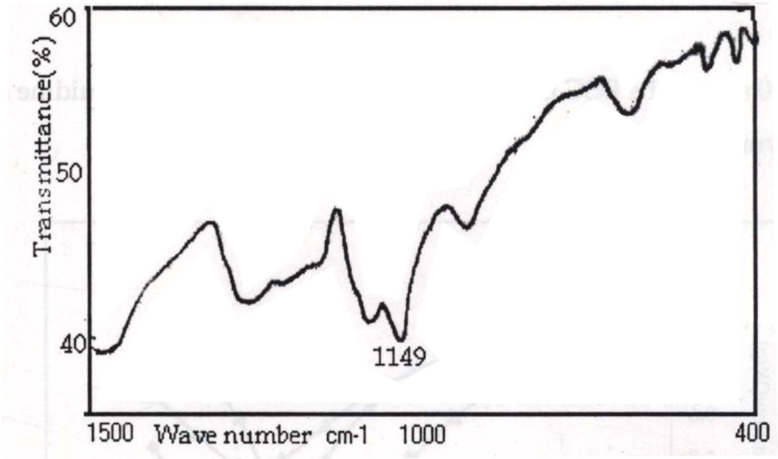


Fig. 4.8: IR spectrum of PoT alone.

The characteristic peak at 1150 cm^{-1} for the conducting Pani and PoT (1149 cm^{-1}) salt are also present in the copolymer (1151 cm^{-1}).

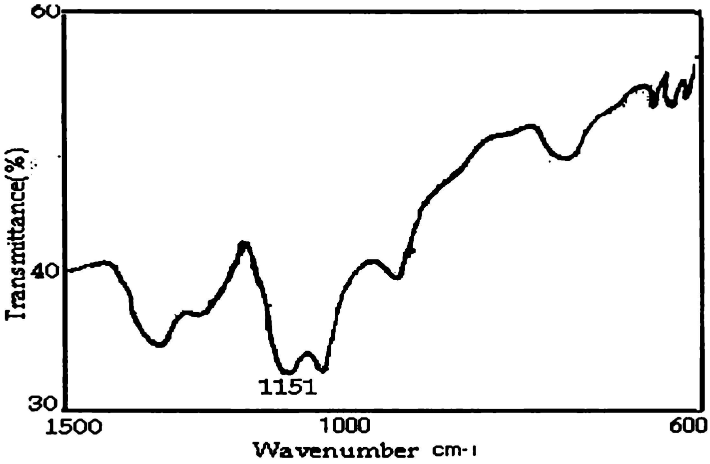


Fig. 4.9: IR spectrum of copolymer.

Figure 4.10 shows the DSC thermogram of polyaniline, Poly o-toluidine and the copolymer.

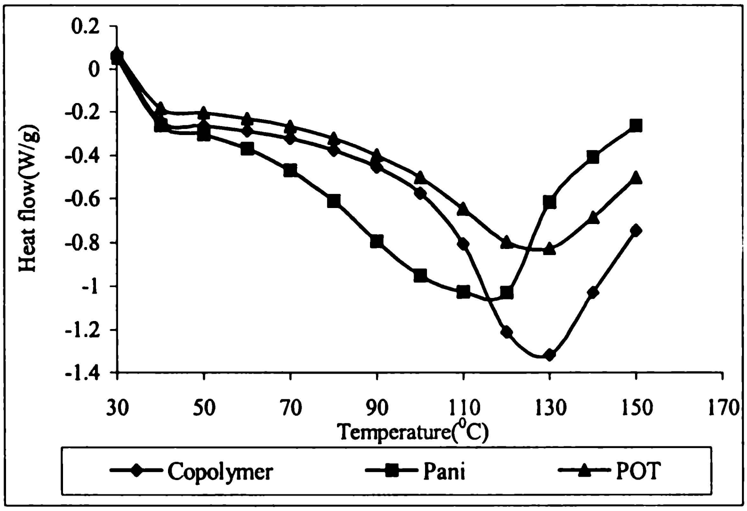


Fig. 4.10: DSC thermogram of Pani, PoT and copolymer.

Here an endothermic peak obtained at 128 ^{0}C in the case of polyaniline and at 130 ^{0}C in the case of poly o-toluidine is shifted to 138 ^{0}C in copolymer. The peak of the copolymer shows intensity between PoT and Pani, also proves the formation of a copolymer.

(b) Effect of drying conditions

The conductivity of the copolymer is also higher for oven dried sample as in the case of poly o-toluidine alone (figure 4.11).

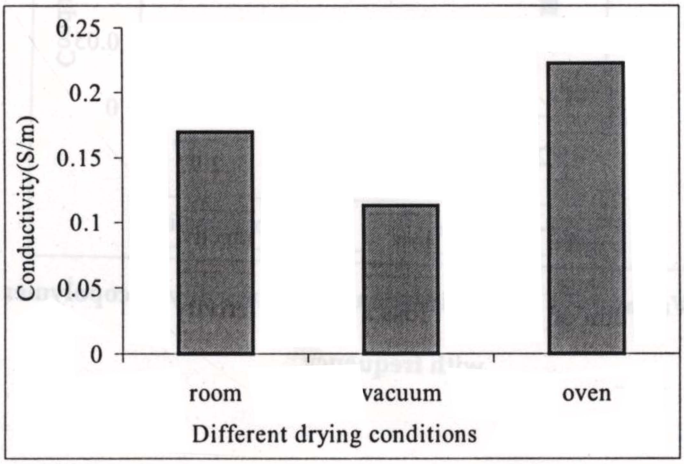


Fig.4.11: Variation of conductivity of copolymer with drying conditions at 2.97 GHz.

(c) Variation of dielectric properties with frequency

1. Dielectric loss and conductivity

Dielectric loss and conductivity increase with increase in frequency (figure 4.12). The increase in dielectric loss with frequency is due to the frictional loss at higher frequencies as in the case of polyaniline. Since the conductivity is directly related to the dielectric loss factor, it also shows the same effect.

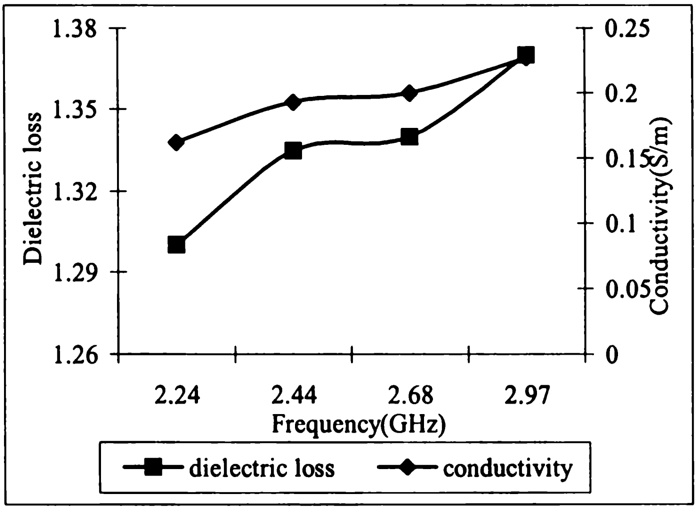


Fig.4.12: Variation of dielectric loss and conductivity of copolymer with frequency

2. Dielectric constant

The dielectric constant is found to decrease with an increase in frequency as shown in figure 4.13. The orientation polarization in an a.c. field results in a decrease in dielectric constant (ε_r') with frequency, as explained earlier.

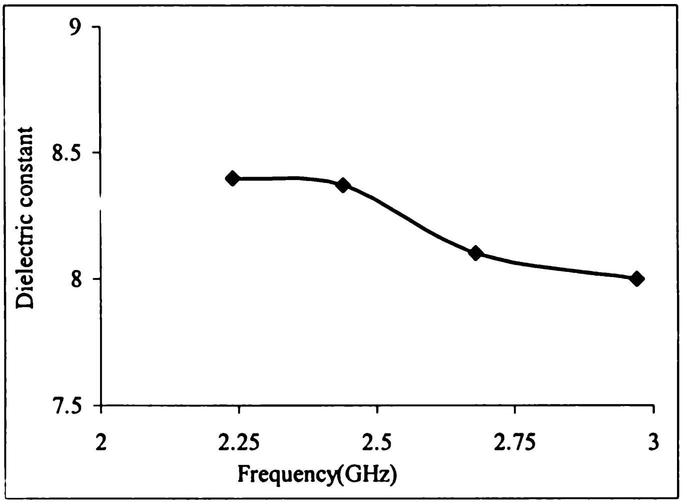


Fig.4.13: Variation of dielectric constant with frequency

3. Dielectric heating coefficient and loss tangent

Dielectric heating coefficient decreases with increase in frequency as shown in figure 4.14. The lower the heating coefficient, the better will be the material for heating applications. Figure 4.15 shows the variation of loss tangent with frequency. Loss tangent is directly related to the dielectric loss factor and it increases with increase in frequency.

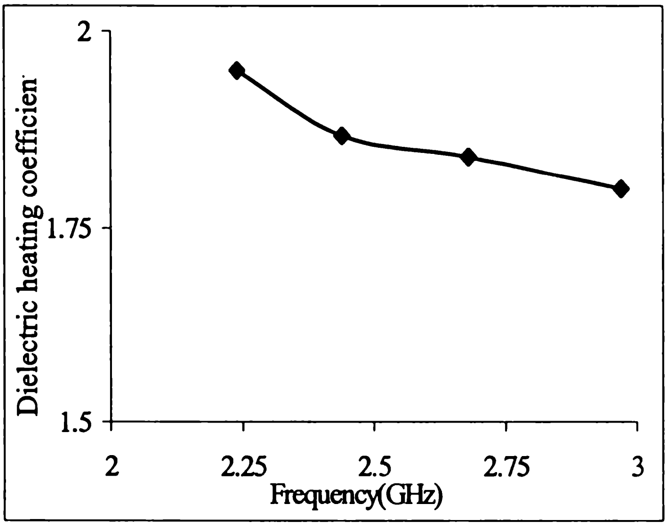


Fig 4.14: Variation of dielectric heating coefficient of copolymer with frequency

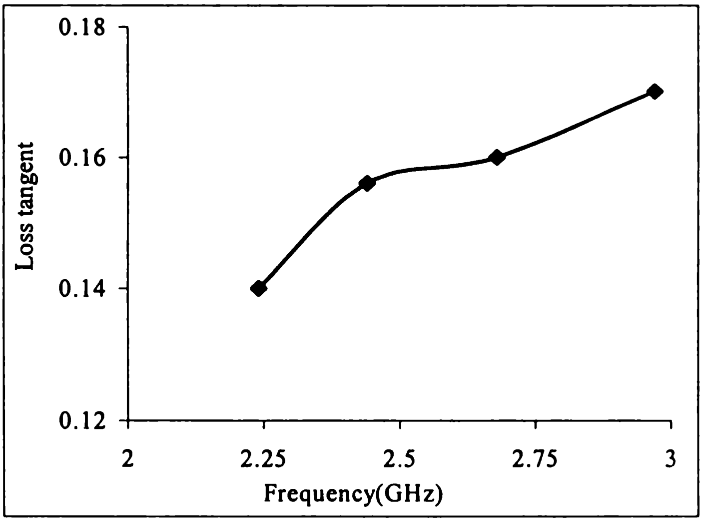


Fig 4.15: Variation of loss tangent of copolymer with frequency.

4.2.3.Comparison of dielectric properties of PoT, Pani and Poly(o-toluidine co aniline)

Fig 4.16 gives a comparison of dielectric properties like dielectric loss and conductivity of PoT, Pani and the copolymer at 2.97 GHz. Dielectric loss and conductivity is found to be higher for polyaniline. Also the copolymer shows higher dielectric loss and conductivity when compared to that of PoT. The introduction of a substituent group (-CH_3 group in o-toluidine) would 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 in reduced conductivity[25]. Also the sterric effect of -CH_3 increases the interchain distance and as inter chain hopping becomes difficult, the conductivity level is lowered[33]. When the copolymer is prepared, a part of the poly *o*-toluidine is replaced with highly conducting polyaniline, which inturn increases the conductivity of the copolymer.

The dielectric constant is found to be higher for the copolymer and polyaniline (figure 4.17). It is also clear from the figure that the heating coefficient (J) is less for the copolymer. In the case of poly o-toluidine the steric hindrance increase the inter chain distance and it decreases the capacitive coupling between the chains. This will leads to a lower dielectric constant. The dielectric heating coefficient is inversely related to the dielectric loss. As the dielectric loss of Pani and the copolymer are high compared to poly o-toluidine, the dielectric heating coefficient shows a lower value for Pani and copolymer.

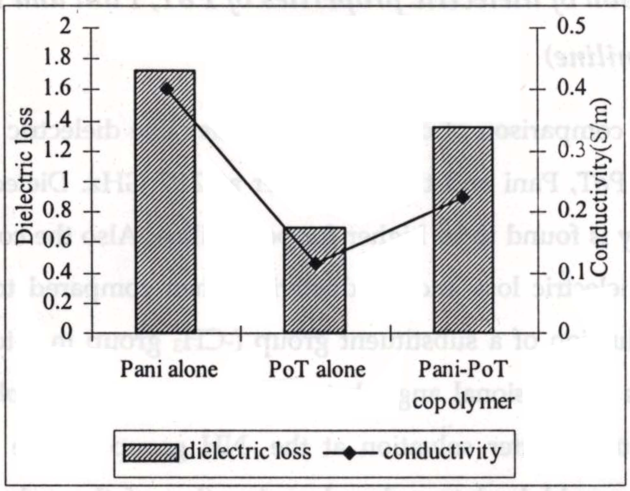


Fig 4.16: Variation of dielectric loss and conductivity with material at 2.97 GHz

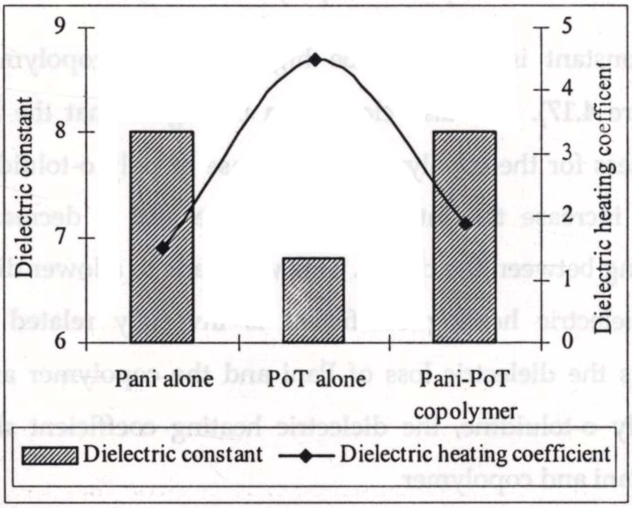


Fig 4.17: Variation of dielectric constant and J with material at 2.97 GHz.

Table 4.1 shows the absorption coefficient and skin depth of Pani, PoT and that of copolymer. It is clear from the table that the absorption coefficient is high for polyaniline and low for poly o-toluidine. The copolymer shows an intermediate value. The absorption coefficient is directly related to the loss factor. Since polyaniline and copolymer shows higher dielectric loss compared to poly o-toluidine, the absorption coefficient of Pani and the copolymer are high. The table also shows that the skin depth is less for polyaniline alone and copolymer. Therefore the copolymer is more opaque to electromagnetic radiation when compared to poly o-toluidine.

Table 4.1: Absorption coefficient and skin depth at 2.97GHz.

	Pani Alone	PoT Alone	Copolymer
Absorption coefficient(m^{-1})	30	8.1	14.72
Skin depth(m)	0.05	0.12	0.07

(d) TGA studies

Figure 4.18 shows the TGA thermogram of polyaniline, POT and copolymer. It is clear from the figure that the Pani shows a weight loss of 18 % up to 150 ^{0}C and POT alone shows 8% loss up to 150 ^{0}C. The initial loss of copolymer is in between Pani and POT i.e., 10% up to 150 ^{0}C. The initial loss is due to the evolution of dopant molecule. It is clear that the dopant concentration in Pani is higher when compared to POT and copolymer because the -CH_3 group in the POT may restrict the higher percentage of doping in POT. The second loss is same in all cases, from 300 ^{0}C and it shows a continuous degradation from that temperature.

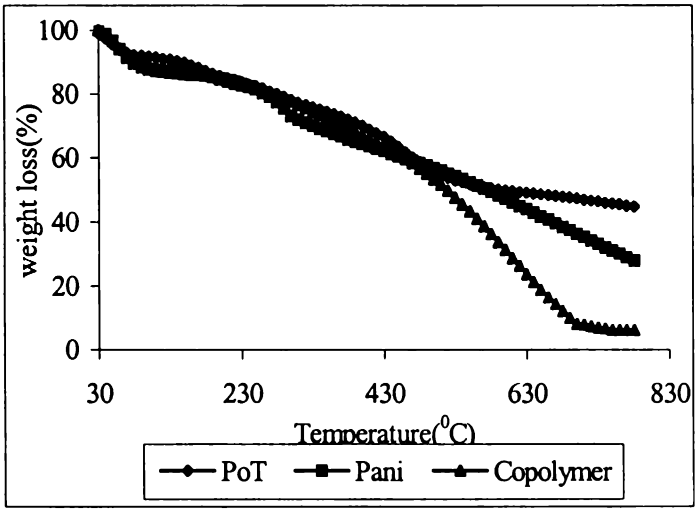


Fig.4.18: TGA Thermogram of POT, Pani and Poly (o-toluidine co aniline).

PART II

4.3 STUDIES ON POLY o-TOLUIDINE - POLYVINYL CHLORIDE COMPOSITES

4.3.1. Studies on Poly o-Toluidine / Polyvinyl Chloride Semi interpenetrating networks (PoT/PVC) in pellet and film forms

Conducting polymers especially polyaniline and its analogues find very good applications in industrial, scientific and medical fields. But the main draws back of these conducting polymers are its processing difficulty. When poly o-toluidine is prepared, the solubility of the conducting polymer is increased due to the presence of a substituent group. But the real fact is that it will contribute very little to the processing. So we have prepared PoT-Polyvinyl chloride semi inter penetrating networks (PoT:PVC SIPN) to improve the processability. In this part we report the synthesis and characterization of PoT-PVC SIPN in pellet and film forms and its dielectric properties at microwave frequencies. Also the degradation of SIPN's are presented.

4.3.1.1. EXPERIMENTAL

- ***Materials Used***

1. o-toluidine (reagent grade) is distilled prior to use.
2. Ammonium per sulphate, emulsion grade Polyvinyl chloride and cyclohexanone used are analar grade.

♦ *Preparation of Poly o-toluidine / Polyvinyl chloride SIPN in pellet form.*

Chemical oxidative polymerization of o-toluidine is carried out using ammonium per sulphate as initiator in the presence of emulsion grade polyvinyl chloride and 1M HCl. The polymerization is carried out for 4 hrs. at room temperature. It is then filtered, washed and dried in an oven at 50 - 60 ^{0}C for 6hrs. (Since the oven dried samples shows better properties as shown in part 1) and is then pelletized. The dielectric properties of these SIPN's are measured using cavity perturbation technique. Different compositions of PoT:PVC SIPN's, say, 1:.5, 1:1, 1:2,1:3,1:4 are prepared using the above procedure and the dielectric properties are measured.

♦ *Preparation of cyclohexanone soluble PoT:PVC SIPN*

Chemical oxidative polymerization of o-toluidine is carried out using ammonium per sulphate as initiator in the presence of emulsion grade polyvinyl chloride solution in cyclohexanone. The polymer formed is then made into film by solution casting and is doped with 1M HCl. Different compositions of PoT-PVC SIPN's say, 2:1, 1:1, 1:2,1:3 and 1:4 are prepared using the above procedure. Here the dielectric study is conducted in three bands, S, C and X bands.

4.3.1.2. RESULTS AND DISCUSSION

(a) Dielectric properties of pellet samples

1. Dielectric Conductivity

Fig. 4.19 shows the variation of the dielectric loss of different SIPN's in pellet form at S band. It is found to increase with increase in frequency.

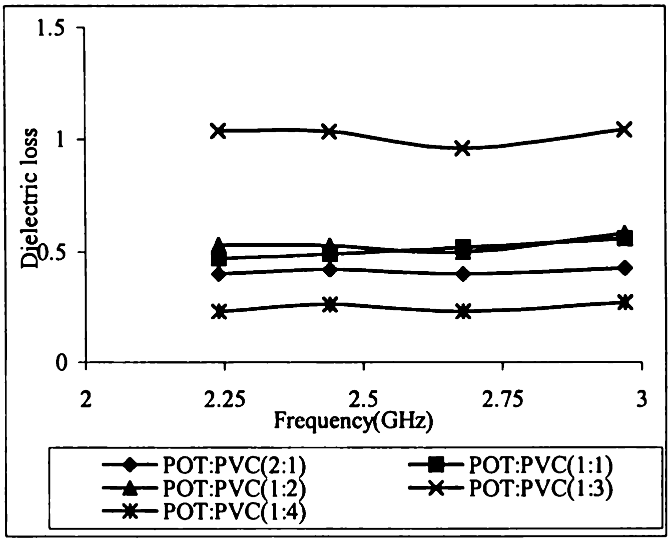


Fig 4.19 : Variation of dielectric loss (PoT:PVC) SIPN with frequency.

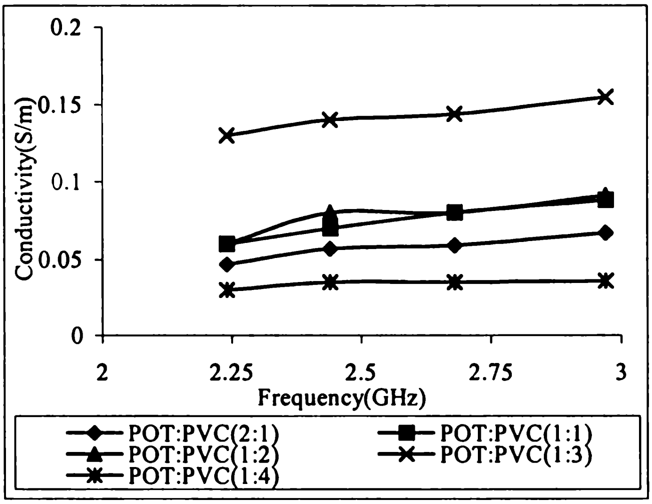


Fig 4.20 : Variation of conductivity of PoT:PVC SIPN's with frequency

At higher frequencies the rotational displacement of polar groups in an a.c. field generates a high dielectric loss[34]. Figure 4.20 shows the conductivity of different SIPN's with frequency and as it is directly related to the dielectric loss factor, it shows the same behaviour.

2. Dielectric constant

It is clear from the figure 4.21 that the dielectric constant decreases with increase in frequency as expected. It is due to the orientation polarization in the microwave field.

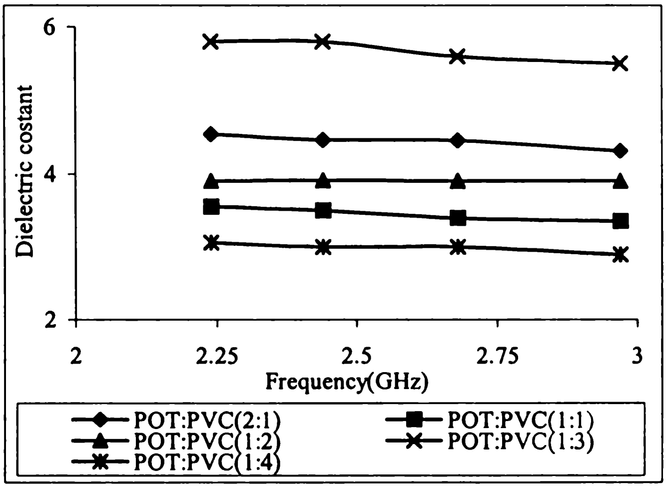


Fig 4.21: Variation of dielectric constant of PoT:PVC SIPN's with frequency.

As the frequency of the applied field is increased, the net polarization is reduced to orientation polarization[31] and this fall in polarisability leads to a decrease in dielectric constant. In other words, at higher frequencies due to the rotational displacement of polar groups under the influence of an a.c. field, frictional loss increases and it reduces the dielectric constant[35].

3. Dielectric heating coefficient(J)

The variation of dielectric heating coefficient with frequency is shown in figure 4.22. The figure shows that there is a slight decrease in dielectric heating coefficient with increase in frequency.

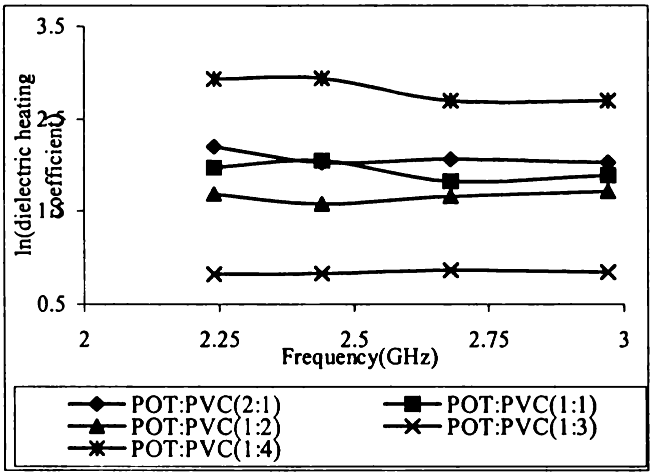


Fig 4.22: Variation of dielectric heating coefficient of PoT:PVC SIPN's with frequency.

(b) Variations of dielectric properties with compositions

The dielectric loss and conductivity increases with PVC loading and reaches a maximum at 1:3(POT:PVC) composition and then decreases as shown in figure 4.23.

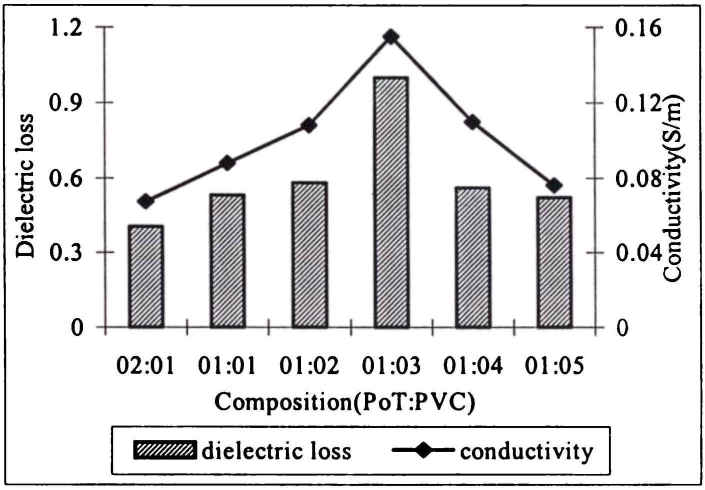


Fig.4.23: Variation of dielectric loss and conductivity with composition of PoT:PVC at 2.97 GHz.

The reason for this behavior is the same as explained earlier. In short, the quantity and geometry of the PVC at 1:3 proportion is more favorable for the high dielectric loss and conductivity.

Figure 4.24 shows that the dielectric constant decreases with increase in PVC loading. The introduction of weakly polar PVC will decrease the dielectric constant. It is also clear from the figure that the dielectric heating coefficient decreases with increase in PVC content and it reaches a minimum value at 1:3 (PoT:PVC) composition. This composition is suitable for the dielectric heating applications.

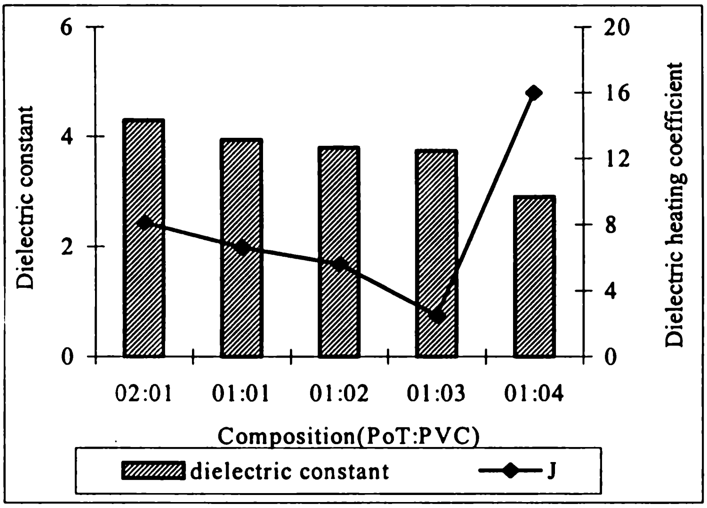


Fig 4.24: Variation of dielectric constant and dielectric heating coefficient with composition of PoT:PVC at 2.97 GHz.

4. Absorption coefficient and skin depth

Table 4.2 shows the absorption coefficient and skin depth of different compositions of PoT:PVC SIPN's at 2.97 GHz. It is clear that the absorption coefficient is high and skin depth is low for 1:3 PoT:PVC composition. The absorption coefficient is highly dependant on the loss factor and since the 1:3 composition gives the highest loss factor, the absorption coefficient is also high. Skin depth or penetration depth is inversely related to the loss factor.

Table 4.2: Absorption coefficient and skin depth of PoT:PVC SIPN at 2.97 GHz

	Composition(PoT:PVC)				
	2:1	1:1	1:2	1:3	1:4
Absorption coefficient(m^{-1})	6.02	7	7.82	8	3.88
Skin depth(m)	0.17	0.14	0.13	0.12	0.26

The variation of absorption coefficient and skin depth with frequency is plotted in figures 4.25 and 4.26. The absorption coefficient increases with increase in frequency and skin depth decreases with increase in frequency.

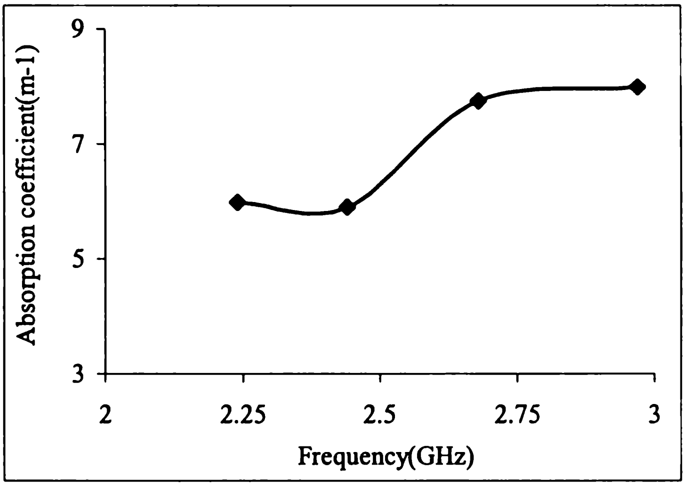


Fig 4.25: Variation of absorption coefficient of 1:3 PoT:PVC composition with frequency.

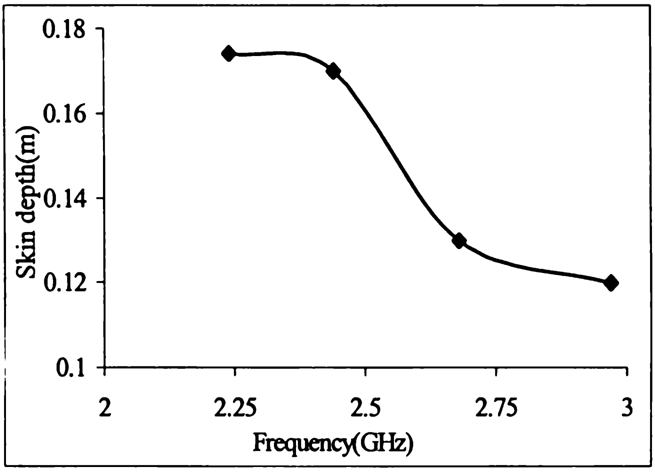


Fig. 4.26: Variation of skin depth of 1:3 PoT:PVC composition with frequency.

(c) TGA studies

The TGA thermograms of PoT, the SIPN's of 2:1, 1:3 and 1:4 (PoT:PVC) compositions are shown in figure 4.27. PoT shows an initial loss of 8% and 2:1 (PoT:PVC) shows 10% at a temperature of 100 - 250 ºC due to the dopant evolution and it is reduced to 5%in the case of 1:3 and 1:4 (PoT:PVC) compositions. This may be due to the presence of PVC, which may restrict the easy evolution of dopant molecule. This behaviour is same as in the case of polyaniline. The second loss is from 250-400 ºC for about 12% in the case of PoT alone. It is increased to 30% in 2:1 composition due to the degradation of polyvinyl chloride and the conducting polymer. In the case of 1:3, a weight loss of 35% and for 1:4 a weight loss of 55% is observed. This destabilization is due to the higher percentage of PVC and it may be more close to the PoT chain.

After that a continuous degradation of PoT occures.

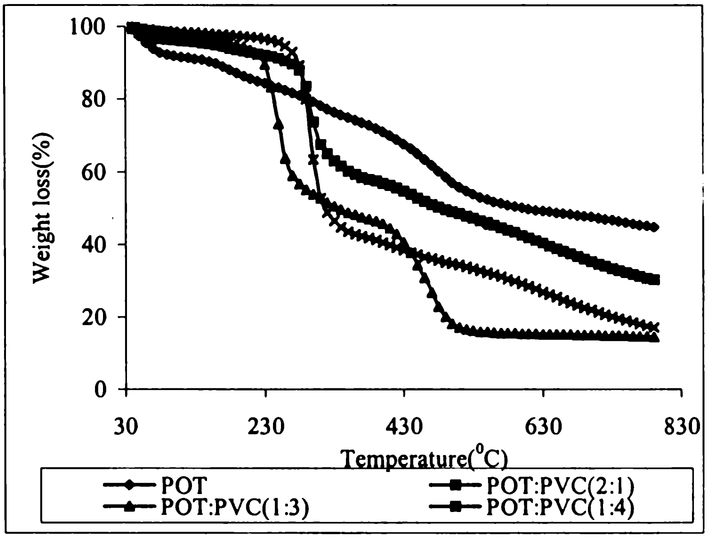


Fig.4.27: TGA thermogram of PoT and its SIPN's.

(d) SEM Studies

Figures 4.28 and 4.29 show the scanning electron micrographs of poly o-toluidine and its SIPN of 1:3 PoT:PVC composition in powder form. It is clear from the figures that the PoT is not densely packed (figure. 4.28) and in the SIPN it makes an interpentrating network with PVC (figure.4.29).

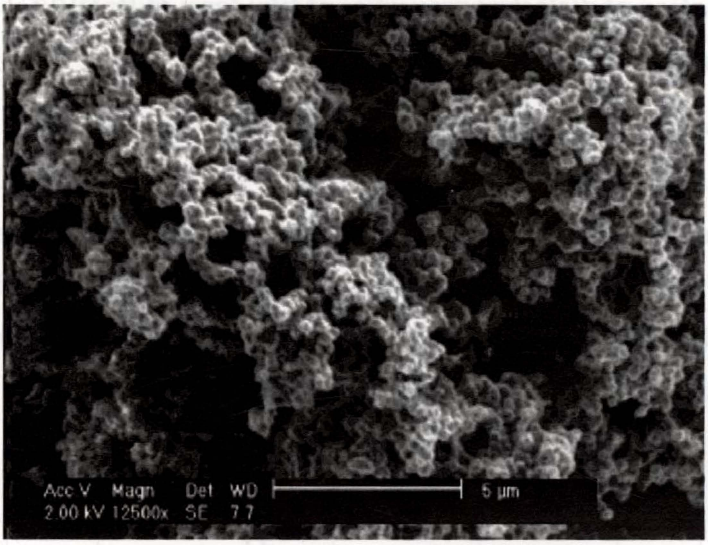


Fig.4.28: Scanning electron micrograph of PoT alone.

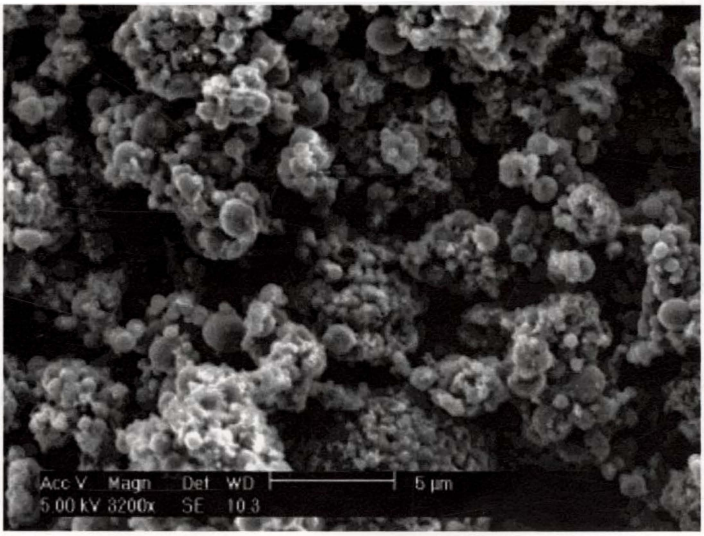


Fig.4.29: Scanning electron micrograph of PoT:PVC SIPN.

(e) *Variation of dielectric properties of film form of PoT:PVC SIPN with compositios*

Figure 4.30 shows the dielectric loss and conductivity of different compositions of PoT:PVC SIPN's in film form at S band. It is very interesting that the dielectric loss and conductivity are higher for 1:3 composition as in the case of pellet form of the SIPN. Also the figure 4.31 shows that this composition is better for dielectric heating applications since it shows the minimum heating coefficient.

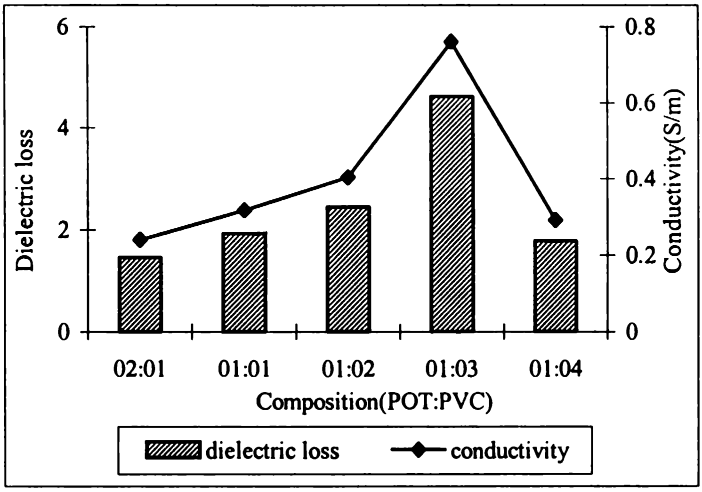


Fig 4.30: Variation of dielectric loss and conductivity with compositions of PoT:PVC at 2.97 GHz.

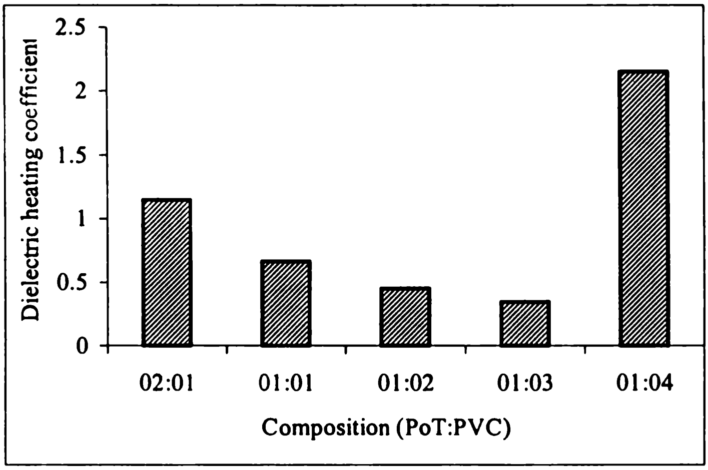


Fig. 4.31: Variation of dielectric heating coefficient with compositions of PoT:PVC at 2.97 GHz

(f) Variation of dielectric properties of film form of SIPN with frequency

1. Dielectric loss and conductivity

Dielectric loss and conductivity of 1:3 composition of PoT:PVC SIPN in film form against frequency is plotted in figure 4.32. It is clear from the figure that the dielectric loss is higher at S band when compared to the C and X bands. When the frequency increases (C and X bands) the dielectric loss decreases due to the rapid rotational displacement of polar molecules under the influence of an a.c. field. At higher frquencies the molecules will not get enough time to get aligned with the field.

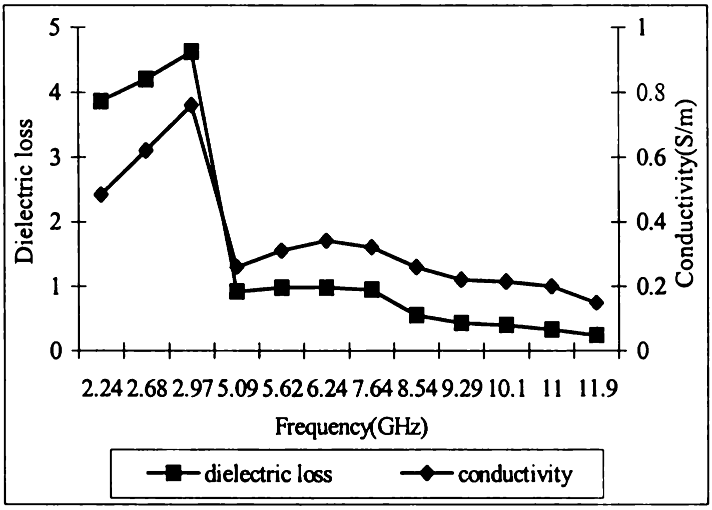


Fig 4.32: Variation of dielectric loss and conductivity of 1:3 PoT:PVC SIPN with frequency.

2. Dielectric constant

The dielectric constant is found to decrease with increase in frequency as shown in the figure 4.33. As explained earlier at very high frequencies the polarization has no longer time to reach its static field value, which reduces the dielectric constant[35].

3. Loss tangent

Figure 4.34 shows the loss tangent (tanδ) of 1:3(PoT:PVC) SIPN at different frequencies. The tanδ is directly related to the dielectric loss factor. Therefore it also shows the same behaviour as that of dielectric loss.

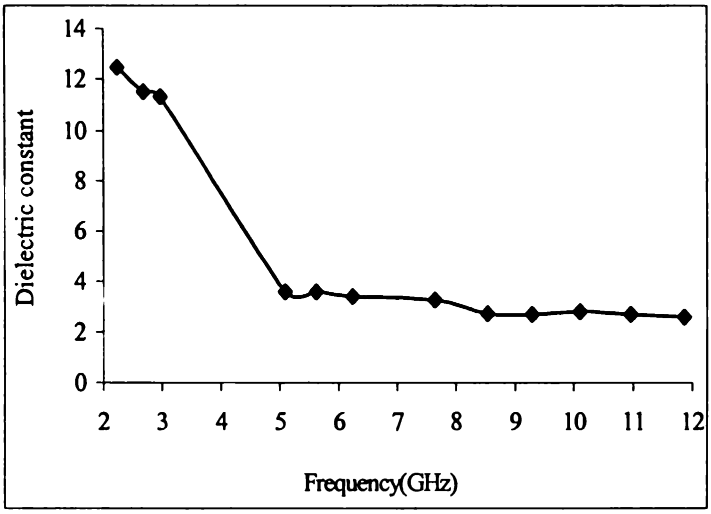


Fig 4.33: Variation of dielectric constant of 1:3 PoT:PVC SIPN with frequency.

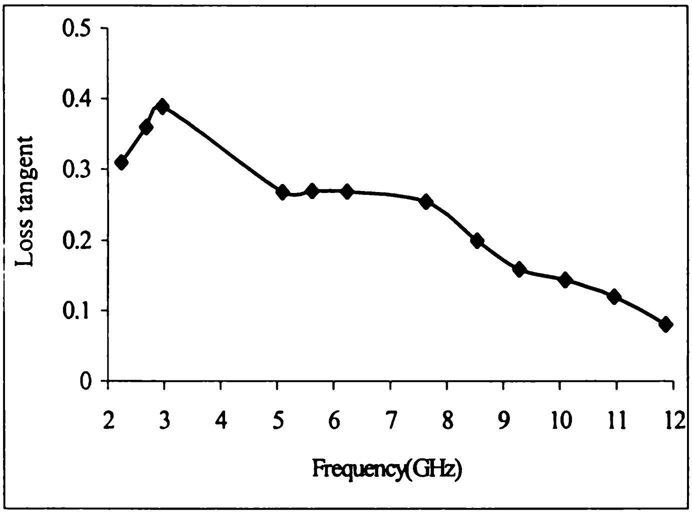


Fig 4.34: Variation of loss tangent of 1:3 PoT:PVC SIPN with frequency.

4. Dielectric heating coefficient(J)

It is observed from figure 4.35 that the SIPN shows very good dielectric heating property, ie, the dielectric heating coefficient is low, in the S band and it is higher for C and X bands. The dielectric heating coefficient is inversely related to the loss tangent and therefore the heating coefficient is higher at C and X bands.

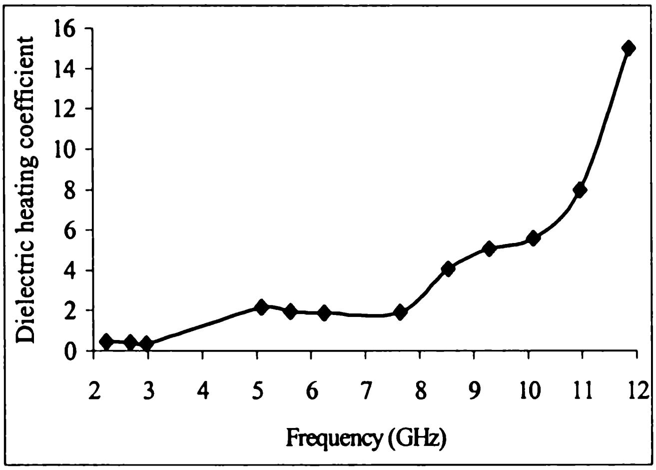


Fig.4.35: Variation of dielectric heating coefficient of 1:3 PoT:PVC SIPN with frequency.

5. Absorption coefficient and skin depth

Table 4.3 shows the variation of absorption coefficient and skin depth of 1:3 PoT:PVC SIPN with frequency. The absorption coefficient is higher at S band when compared to C and X bands. Also the skin depth is lower at S band, makes it useful for shielding applications. But within each band the absorption coefficient increases and the skin depth decreases with increase in frequency.

Table 4. 3 Variation of absorption coefficient and skin depth at S, C and X bands.

	Frequency (GHz)	Absorption Coefficient(m^{-1})	Skin Depth(m)
S band	2.24	25.17	0.04
	2.68	33.17	0.03
	2.97	40.45	0.02
C band	5.09	25.3	0.04
	5.62	29.8	0.031
	6.24	34	0.03
	7.64	35	0.0278
X band	8.54	29.4	3
	9.29	25.4	4
	10.1	26	3
	10.96	26.3	3

4.3.2 Comparison of Pellet and Film Forms

The important dielectric properties like dielectric loss & conductivity of 1:3 proportions of PoT: PVC SIPN's in pellet and film form are compared in figure 4.36. The dielectric loss and conductivity is higher for film samples compared to pellet samples as in the case of polyaniline. The film samples are able to produce more dipolar polarization under the influence of an a.c. field due to its dilution. Due to this the dielectric constant is higher for film as indicated in figure 4.37. The film samples also show minimum heating coefficient (figure 4.37).

The absorption coefficient and the skin depth of pellet and film forms of 1:3 PoT:PVC SIPN are compared in table 4.4. It is seen that the absorption coefficient is higher and the skin depth is lower for the film sample. Therefore the film samples are better for shielding applications.

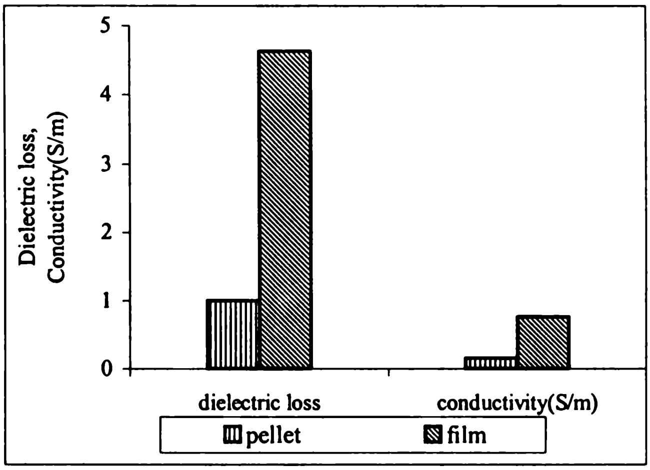


Fig 4.36:Variation of dielectric loss and conductivity with nature of 1:3 PoT:PVC SIPN.

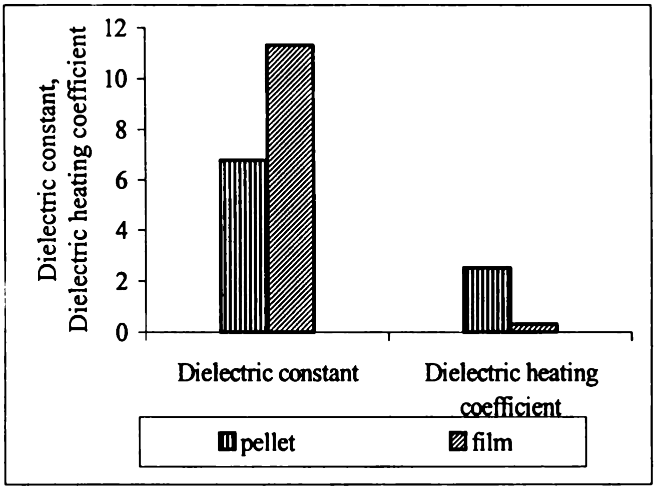


Fig 4.37: Variation of dielectric constant and dielectric heating coefficient with the nature of 1:3 PoT:PVC SIPN.

Table 4.3 : Absorption coefficient and skin depth of (1:3)POT:PVC SIPN at 2.97 GHz

	Pellet	Film
Absorption coefficient(m^{-1})	8	40.45
Skin depth(m)	0.12	0.02

(g) TGA and DSC studies

Figure 4.38 shows the TGA thermogram of pellet and film samples of 1:3 composition. The figure shows that an initial loss of about 6% at a temperature of 100-220 °C for both samples. The second loss of about 44% in the case of pellet sample and 48% for film sample at a temperature of 360

^{0}C. Also a third loss of 28 % in the case of pellet sample is seen at 550^{0}C, but in the case of film samples there is a sharp reduction in the weight observed from 360^{0}C. The higher percentage of weight loss in the case of film samples indicates the more closeness of PVC to the PoT chain.

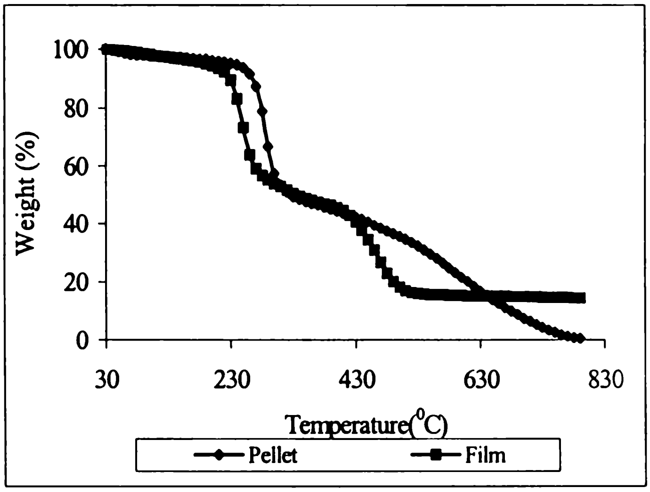


Fig.4.38: TGA thermogram of pellet and film form of 1:3 (POT:PVC) SIPN.

Figure 4.39 shows the DSC of PoT: PVC and SIPN of 1:3 composition in pellet and film forms.

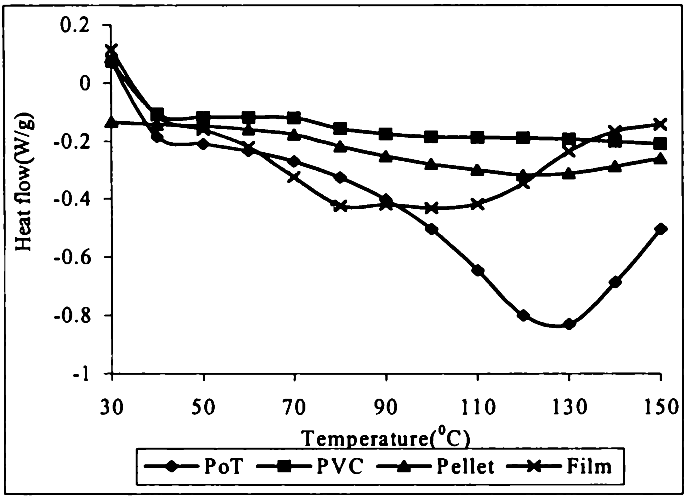


Fig.4.39: DSC thermogram of PoT, PVC and PoT:PVC

1:3 SIPN of pellet and film forms.

It is clear from the figure that the Tg of PoT (130 °C) is shifted to 117 °C in the case of pellet form and to 95 °C in film form. The lower Tg of film sample is an indication of higher flexibility because of the plasticizing action of polyvinyl chloride. This result also proves the higher dielectric properties of film form compared to the pellet form.

4.4.CONCLUSIONS

- The dielectric properties of PoT, copolymer and its SIPN with PVC is related to the frequency.
- The microwave conductivity of all samples are highly dependant upon the dopant concentration.
- In all cases the oven dried samples shows better dielectric properties.
- The dielectric loss and conductivity are higher for the copolymer when compared to PoT.
- The dielectric constant of the copolymer is higher than that of PoT.
- The dielectric heating coefficient is found to be minimum for the copolymer.
- The absorption coefficient is high and the skin depth or penetration depth is low for the copolymer compared to poly o-toluidine alone.
- The conductivity and the dielectric loss increases with increase in PVC loading and it reaches a maximum at 1:3(POT: PVC) proportion in both pellet and film forms.
- The dielectric heating coefficient is found to be minimum for 1:3 composition.
- The absorption coefficient is found to be high for 1:3 composition and the skin depth minimum for that composition.
- The dielectric properties are higher at S band when compared to C and X bands for film samples.

- The film samples show higher conductivity and absorption coefficient values than pellet samples.
- The dielectric heating coefficient and penetration depth are lower for film samples.
- The dielectric constant is found to higher for the film samples.
- The processing difficulty can be over come by preparing the film sample.

4.5. REFERENCES

1. H.Letheby. *J.Chem.Soc.*15,161,(1862).
2. A.G.Green and A.E.Woodhead, *J.Chem Soc.trans.*,97,2388,(1910).
3. A.G.Green and A.E.Woodhead, *J.Chem Soc.trans.*,101,1117,(1912).
4. E. M. Genies, A. Boyle, M. Lapkowski and C. Tsintavis, *Synth.Metals*, 36, 139, (1990).
5. J.P. Travers, F. Genoud, C. Menardo and M. Nechtschein, *Synth.Metals*, 35, 159, (1990).
6. N. Li. Lee and L. H. Ong. *J.Appl.Electrochem.* 22,512, (1992).
7. F.Trinidal, M.C. Montemayer and E. Falas. *J. Electro chem.Society* 138,3186, (1991).
8. A.J.Epstein and A.G.MacDiarmid, Faraday Discuss. *Chem. Soc.*,.88,317(1989).
9. A.G.MacDiarmid and A.J. Epstein, *J.Chem.Soc.Faraday Disc.*, 88,317,(1989).
10. F.Lux,, 35,2915,(1994).
11. M.Leclerc, J.Guay and L.H.Dao, *Macromolecules*, 22,649,(1993).
12. M.Leclerc, J.Guay and L.H.Dao, *J.electroanal.Chem.*, 251,21,(1988).
13. J.Anand, S.Palaniappan and D.N.Sathyanarayana, *Synth.metals.*,63,43,(1994).
14. J.Anand, S. Palaniappan and D.N. Sathyanarayana, *Synth.metals.*, 66, 129, 1994).
15. K.Lee, A.J.heeger and Y.cao, *Phys.Rev.*,B48,14884,(1993).

16. Z.H. Wang, H.H.S. Javadi, A. Ray and A.G. MacDiarmid, *Phy.Rev.*, **B42,** 5411, (1990).

17. Z.H. Wang, H.H.S. Javadi, A. Ray ,A.G. MacDiarmid, and A.J. Epestein, Phy.Rev., **B43**,4373,(1991).

18. Z.H. Wang, E.M. Scherr, A.G. MacDiarmid, and A.J. Epestein, *Phy.Rev.*, **B45**, 4190,(1992).

19. Y.Z.Wang,J.Joo, C.H.Hsu and A.J.Epstein, *Synth.Metals*, **68**,207(1995).

20. H.H.S. Javadi, K.R. Cromack, A.G. MacDiarmid, and A.J. Epestein, *Phy.Rev.*, B39, 3579,(1989).

21. M.F.Jozeefowiez, A.J.Epestein, J.P.Pouget, J.G.Masters, A. Ray and A.G. MacDiarmid, *Macromolecules*,**24**,5863,(1991).

22. C.Ku. Chen, and Raimond Liepins, *Electrical properties of polymers*, Hanser publications, New York (1987).

23. Jayasree Anand, S.Palaniappan and D.N.Sathyanarayana, *Hand book of organic conductive molecules and polymers*, **Vol.2**, Chapter 13, H.S.Nalwa,Wiley & Sons Ltd.

24. V. Saravanan,.; S .Palaniappan, S. Seetharamu, *Macromol New Frontiers* **1**, 374, 1998

25. Meenakshi Maruthamuthu, G.Harichandran and D.Jeyakumar, *Macromolecules New Frontiers*, **Vol.1**, 359, 1998

26. John Honey,S.Bijukumar,K.T.Mathew and Joseph Rani, *J.Appl.Polym.Sci.*, **83**, 2008-2012,2002.

27. P.Kathirgamanathan, P.N.Adams, K.Quill, and E.Underhill,*J.Mater.Chem.*,1, 141(1991).

28. Y.Wei, A.Hariharan and S.A.Patel, *Macromolecules* **23**,758(1990).
29. S.K.Dhawan and D.C.Trivedi, *Synth.Met.***60**, 63(1993).
30. J.Y.Bergeron and L.H.Dao, *Macromolecules,* **25**,3332(1992).
31. Z.H.Wang et al., *Phys.Rev.B, Condens.Matter.,* **43**,5373,(1991).
32. S.Ye, S.Besner, L.H.Dao and A.K.Vijh, *J.Electroanal.Chem.***381**, 71(1995).
33. L.Olmedo, P.Hourquebie and F.Jousse, *Hand book of organic conductive molecules and polymers,* **Vol.3**, Chapter 8, Edited by H.S.Nalwa, John Wiley(1997).
34. N.G.McCrum,B.Ee. Read, G.Williams, Anelastic *Dielectric Effects in Polymer solids,* John Wiley & Sons Ltd., London, 1967
35. J.C.Maxwell, *Electricity and Magnetism,* Oxford University Press, Oxford (1892)

Chapter 5

STUDIES ON POLY PYRROLE AND ITS COMPOSITES

5.1 INTRODUCTION

In recent years conducting polymers with conjugated double bonds have attracted much attention as advanced materials. Polypyrrole (PPy) is especially promising for commercial applications because of its good environmental stability, facile synthesis, and higher conductivity than many other conducting polymers. PPy can often be used as biosensors[1,2], gas sensors[3,4], wires[5], microactuators[6], anti electro static coatings[7], solid electrolytic capacitor[8,9], electro chromic windows and displays and packaging, polymer batteries, electronic devices and functional membranes etc[10-12]. PPy coatings have an excellent thermal stability and are good candidate for use in carbon composites[13].

PPy can be easily prepared by either chemical or electrochemical polymerization of pyrrole. In the past decade many reports about PPy have been published[14]. At the same time, the relationships between the properties and the polymerization conditions, PH value[15] were also studied. Biswas and

Roy[16], studied the thermal stability and morphological and conductive characteristics of the PPy prepared in aqueous medium. The results showed that the PPy exhibits a spongy texture, with the initial decomposition temperature at 180-237 °C, glass transition temperature at 180-170 °C and conductivity below 3 S/m. All results depend upon the FeCl3 / pyrrole feed composition. In a recent report, PPy films of thickness 3-4 μm have been obtained by chemical oxidation of pyrrole at the interface of chloroform and water with an oxidant ammonium per sulfate[17]. The surface morphology of PPy film has also been studied through atomic force microscopy[18, 19].

Several investigations[20, 21] have been performed to observe the effect of various parameters such as solvent, electrolyte choice of monomer, polymerization temperature, annealing temperature on the mechanical strength, stability and conductivity of the PPy films prepared. Surface morphology studies show that a 3D-type growth and an increase in handly strength after a certain annealing time [21].

Sacak et al prepared PPy/polyaniline films on platinum foil electrodes by sequential electrode sides of the films[22]. It was found that depending upon conditions, either the second polymer was incorporated into the initially coated layer or a double layer film was formed with a well-defined interface. Conducting electroactive polymer membranes such as PPy membranes have attracted much interest over the past decade because of their dynamic, chemical and electrochemical properties. Zhao et al[23], synthesized asymmetric membranes based on conducting polypyrrole. In recent years, composite membranes based PPy were also studied[24,25].

However synthetically conductive PPy is insoluble and infusible, which restricts its processing and applications in other fields. To improve the processability many researchers have been engaged in the development of soluble or swollen PPy and dispersible fine powdered PPy. Several kinds of soluble PPy have been synthesized, such as poly (3-alkyl pyrrole) with an alkyl group equal to or greater than a butyl group[26]. Another way to improve the processability is the preparation of blends or composites. When a comparison is made among the three conducting polymer polyaniline, polythiophene and polypyrrole, PPy can form blends easily with the insulating polymers. As for PPy, it has a high conductivity and good environmental stability, but poor mechanical properties. This has been overcome to some extent by use of composite structures, for example, combination of the PPy film with insulating polymers such as poly-N-vinyl carbazole[27], polystyrene[28], polyvinyl phospate[29], polyvinyl alcohol[30] and so on. The conducting composite films are prepared either by electrochemical polymerization of pyrrole on an electrode substrate whose surface is coated with an ordinary insulating polymer film[31] or by exposing a polymer film containing an oxidizing agent such as ferric or cupric chloride to pyrrole vapour[32]. In the first case film consist of two or three layers with the polymer sandwiched between two layers of polypyrrole. In the second case the polypyrrole particles are dispersed in polymer film. In both cases it cannot be changed in to other shapes and therefore the application areas are limited.

Another method to improve its processability is the synthesis of block and graft copolymers containing conventional and conducting sequences, where by conventional sequence improves the solubility of the resultant block [33]. Many studies on PPy film were published. Teike and Gabriel studied pyrrole-polyimide composite films[34]. It was reported that the composite films had high electrical conductivity with high thermal stability. The research by Kaynak et al [35] proved that the electrical conductivity of the doped polypyrrole films has a significant effect on transmission, reflection and absorption of microwaves. Heavily doped conducting polymer films were highly reflective whereas lightly doped films had very high transmission. Intermediate conductivity samples were highly absorptive.

In this chapter we report the synthesis, characterization, degradation studies and dielectric properties of polypyrrole. An alternative route for the preparation of polypyrrole to improve the dielectric properties in the microwave frequencies is also included. Also to improve the processability conductive semi inter penetrating polymer networks based on polypyrrole - polyvinyl chloride are prepared, in various forms and its properties are studied.

PART 1

5.2. STUDIES ON POLYPYRROLE AND ITS SIPN WITH POLYVINYL CHLORIDE USING $FeCl_3$ AS INITIATOR

Incorporation of conducting polymer into a host polymer substrate forming a blend, composite or inter penetrated bulk network has been widely used as an approach to combine electrical conductivity with desirable physical properties of polymers[34,35] . Polypyrrole is considered as one of the most promising candidate for the fabrication of conductive blends / composites/inter penetrating networks (IPN's) with industrially important class of polymers [36].

IPN conducting composites result through in-situ polymerization[37-40] of monomers of conducting polymers inside the matrices of the conventional linear polymers by chemical or electrochemical methods of polymerization. Eventhough numerous studies were done on polypyrrole and its composites in the d.c. field, we are reporting the microwave dielectric properties of poly pyrrole (PPy) and polypyrrole-polyvinyl chloride (PPy-PVC) semi interpenetrating networks (SIPN's). Cavity perturbation technique is used for the study.

5.2.1 EXPERIMENTAL

- **Materials Used**

1.Pyrrole (reagent grade) & methanol are distilled prior to use.

2.Ferric chloride, emulsion grade Polyvinyl chloride are used as received.

- **Preparation of Polypyrrole**

Polypyrrole is prepared by the polymerization of pyrrole with ferric chloride[41] in the presence of methanol. The reaction is carried out for 20 minutes at 0-5 ^{0}C. It is then filtered, washed and dried under vacuum for 16 hrs. at room temperature.

- **Preparation of Polypyrrole / Polyvinyl chloride Semi Inter penetrating network**

Polypyrrole / Polyvinyl chloride (PPy/PVC) SIPN is prepared by the polymerization of pyrrole with ferric chloride in the presence of methanol and emulsion grade polyvinyl chloride. The reaction is carried out for 20 minutes at 0-5 ^{0}C. It is then filtered, washed and dried under vacuum for 16 hrs. at room temperature. Different compositions of PPy-PVC composites, say, 3:1, 1:1, 1:1.5, 1:2, 1:2.5, 1:3 are prepared using the above procedure and the dielectric properties are measured.

In this part of study we are using the conventional method for drying, i.e., vacuum drying as the drying condition has little effect on the dielectric properties.

5.2.2 RESULTS AND DISCUSSION

(a) Variation of dielectric properties with frequency

1. Dielectric loss and Conductivity

Fig. 5.1 shows the variation of the imaginary part of the complex permittivity or the dielectric loss factor ε''_r of polypyrrole and its SIPN's of different proportions with frequency. The dielectric loss is found to increase with increase in frequency in all cases.

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. It is also observed from the figure that there is a dip in the middle frequencies as in the case of polyaniline and poly o-toluidine samples.

The microwave conductivity is a direct function of dielectric loss and hence the figure 5.2 showing the variation of the conductivity of polypyrrole and its SIPN's of different proportions with frequency has the same nature as that of dielectric loss factor.

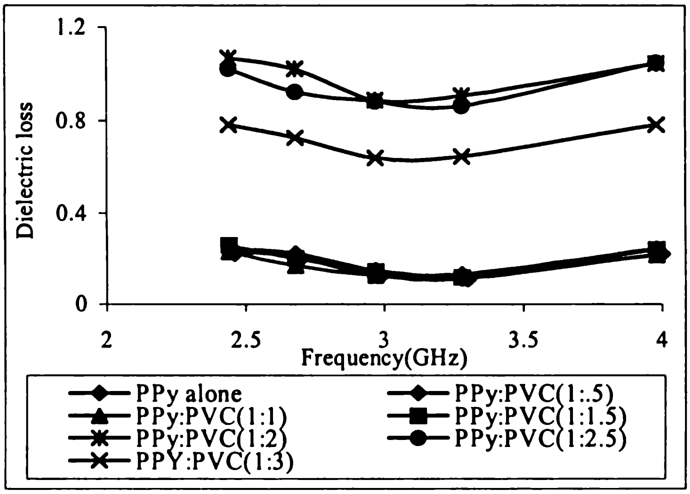


Fig.5.1: Variation of dielectric loss of PPy and PPy:PVC SIPN's with frequency.

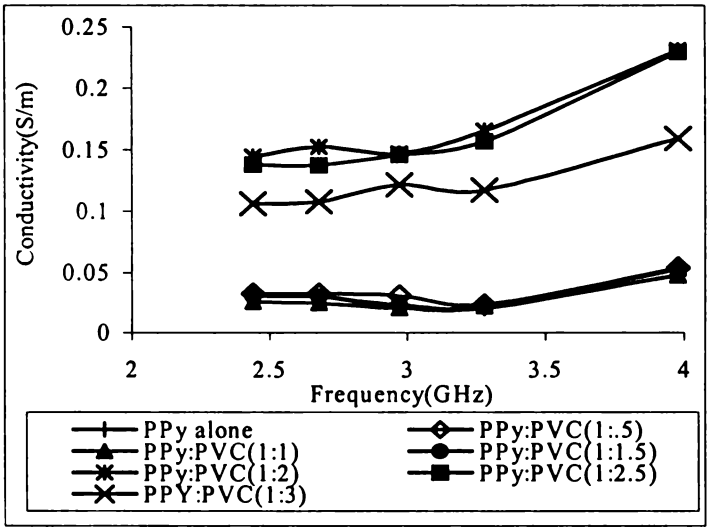


Fig 5.2: Variation of conductivity of PPy and PPy:PVC SIPN's with frequency.

2. Dielectric constant (ε'_r)

Fig 5.3 shows that the dielectric constant decreases with increase in frequency. This is due to the orientation polarization of molecules at high frequencies. Also at higher frequencies, due to the frictional loss caused by the rotational displacement of molecular dipoles the dielectric loss increases and this might results in a decrease in dielectric constant.

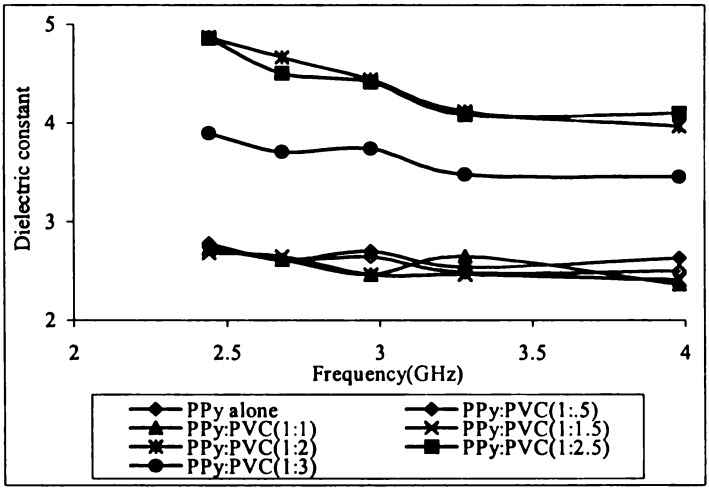


Fig 5.3: Variation of dielectric constant of PPy and PPy:PVC SIPN's with frequency.

3. Dielectric heating coefficient (J)

Fig.5.4 shows the variation of dielectric heating coefficient with frequency. It is observed that the heating coefficient decrease with increase in frequency except for the middle frequency. Higher the J value poorer will be the polymer for dielectric heating purposes.

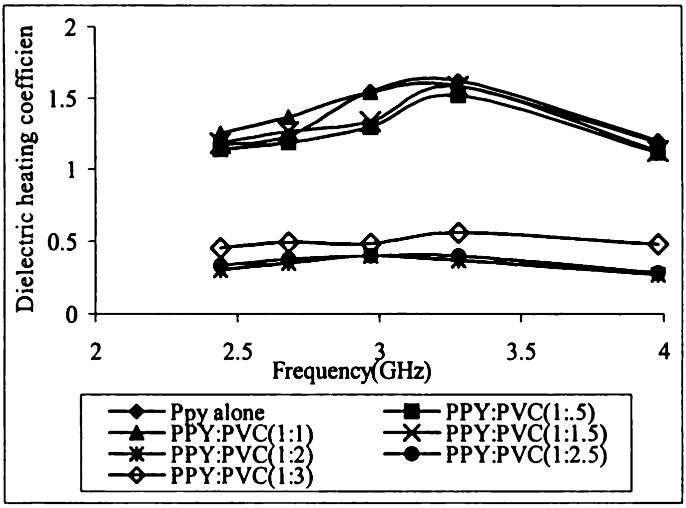


Fig 5.4 : Variation of dielectric heating coefficient with frequency.

(b) Variation of dielectric properties with proportions

1. Dielectric loss and conductivity with composition

Fig. 5.5 shows the variation of dielectric loss and conductivity with different compositions of PPy:PVC SIPN's. It is clear from the figure that the dielectric loss and conductivity is less for polypyrrole and increases with increase in PVC content and reaches a maximum at (PPy: PVC) 1:2 proportion and then decreases. The 1:2 proportion is an optimum composition, which gives high dielectric loss and hence enhanced conductivity due to the easy interchange of polar groups.

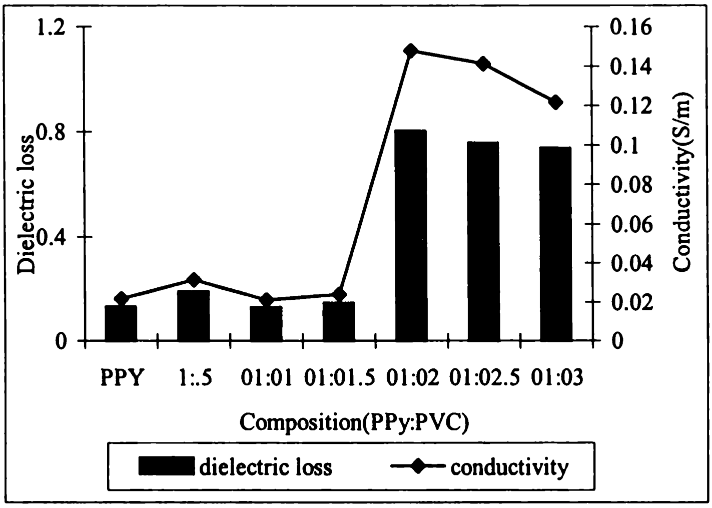


Fig 5.5: Variation of dielectric loss and conductivity with compositions of PPy:PVC SIPN at 2.97 GHz

This is due to the interfacial polarization in the presence of weakly polar polyvinyl chloride as explained earlier.

2. Dielectric constant and dielectric heating coefficient(J)

Fig 5.6 shows the variation of dielectric constant and dielectric heating coefficient with proportions. The dielectric constant is found to decrease with increase in PVC loading. The dielectric heating coefficient (J) is found to be the least for 1:2 proportions and this proportion is an optimum one for dielectric heating purposes.

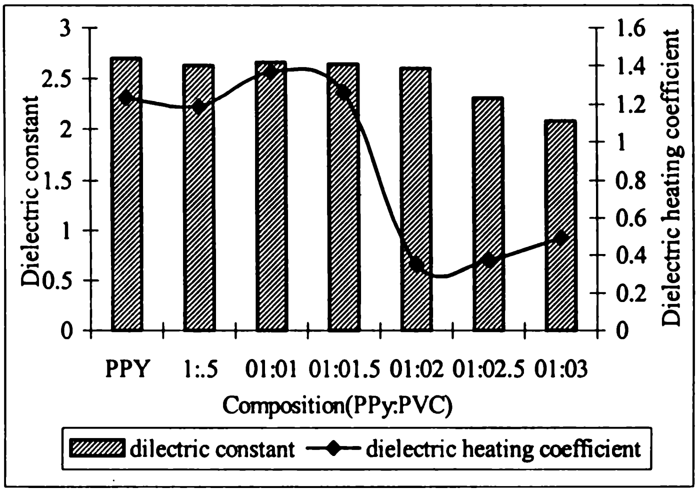


Fig 5.6: Variation of dielectric constant and dielectric heating coefficient with composition of PPy:PVC SIPN at 2.97 GHz.

3. Variation of absorption coefficient and skin depth

Table 5.1 shows the absorption coefficient and skin depth of polypyrrole and different compositions of PPy:PVC SIPN's.

Table 5.1: Absorption coefficient and skin depth of different compositions of PPy:PVC SIPN at 2.97GHz

Property	Composition (PPY:PVC)					
	PPy	2:1	1:1	1:1.5	1:2	1:2.5
Absorption coefficient (m^{-1})	2.46	2.51	3.61	3.78	13.05	11.7
Skin depth(m)	0.41	0.40	0.28	0.26	0.08	0.09

It is clear that the absorption coefficient increases with increase in PVC content and it reaches a maximum for 1:2 proportion as in the case of dielectric loss. Also the skin depth is minimum for 1:2 composition as expected.

Variation of absorption coefficient with frequency is given in figure 5.7. The absorption coefficient is directly related to the dielectric loss factor and therefore it shows the same behavior as that of dielectric loss i.e, the absorption coefficient increases with increase in frequency. Penetration depth or the skin depth decreases with increase in frequency (figure 5.8) as in the case of polyaniline and poly o-toluidine.

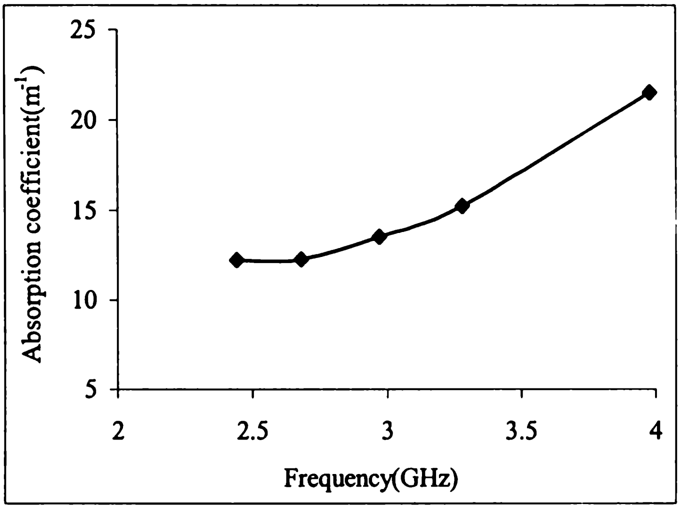


Fig. 5.7: Variation of absorption coefficient with frequency.

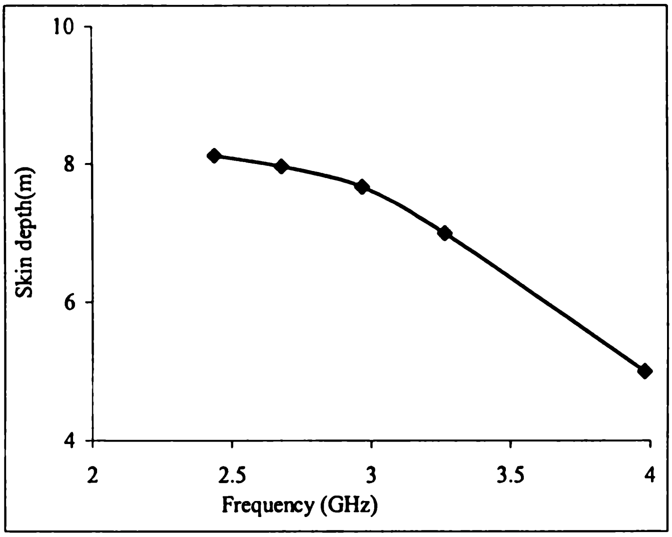


Fig 5.8: Variation of skin depth with frequency.

(c) TGA studies.

The thermograms of polypyrrole, polypyrrole - polyvinyl chloride SIPN's of different proportions like 3:1,1:2 and 1:3 in powder form are shown in figure 5.9. The figure indicates that there is a weight loss of about 12% at 260⁰C due to the evolution of dopant in the case of PPy alone. Then about 56% of weight loss at 426⁰c indicate the degradation of pyrrole and a residue of 23%. In the case of PVC alone, the degradation starts at 272⁰ C (chapter3, figure 3.38), but it is only 4%, due to the evolution of HCl. The degradation of polyvinyl chloride is at 330⁰C for about 50 % and above that temperature there is a sharp decrease in the weight loss curve which indicates the complete rupture of the material. Considering the TGA of PPy: PVC (3:1) SIPN there is a weight loss of 20% at 260⁰C due to the evolution of dopant molecules. This is due to the fact that the stability of polypyrrole is reduced in the presence of PVC. Then at

426^{0}C a weight loss of 25% is observed. In the case of 1:2 composition, only 8% weight loss up to 270^{0}Cand from 270 - 430^{0}C a weight loss of 44% is observed. Also in the case of 1:3 composition there is a reduction in degradation (up to 270^{0}C 9 % weight loss) is observed. The decrease in the degradation in the case of SIPN's is due to the presence of PVC as explained earlier.

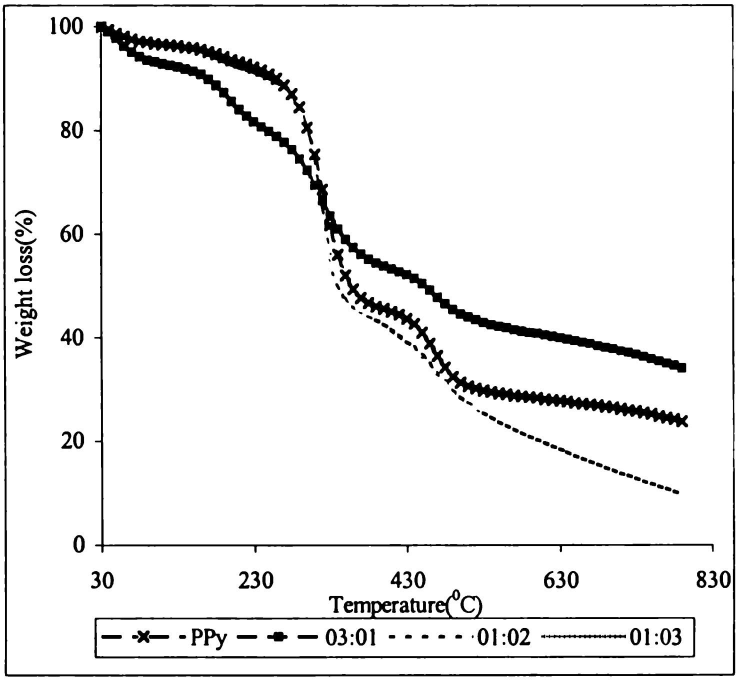


Fig 5.9: TGA thermogram of PPy, PPy: PVC of 3:1,1:2 and 1:3.

PART II

5.3.STUDIES ON POLYPYRROLE AND ITS SIPN WITH PVC USING $(NH_4)_2S_2O_8$ AS THE INITIATOR.

In recent reports, polypyrrole was also prepared using $(NH_4)_2S_2O_8$ as the initiator but the reports indicate that the conductivity is poor when compared to those prepared by normal ($FeCl_3$) initiator. In the microwave study, the conductivity highly depends upon the dopant concentration since the microwave conductivity is due to the dipolar polarization. So we choose $(NH_4)_2S_2O_8$ as initiator to prepare polypyrrole because the reaction is done in the presence of HCl which will increase the dopant concentration. We also studied the effect of different drying conditions on the dielectric properties of polypyrrole. The main drawback of conducting polymer is its processing difficulty. To overcome the processing difficulty, conductive semi inter penetrating networks are prepared with PVC.

The conversion of conducting SIPN into different shapes is not very easy because of the poor binding property of polypyrrole. Also the mechanical property of pellet samples are poor. To overcome these difficulties soluble conducting composite are prepared. The processing of solution is very easy, ie, by solution casting, or it can be easily spin coated, or it can be painted over a surface. The film form of polypyrrole - PVC SIPN is prepared from the uniform solution of the SIPN.

5.3.1 EXPERIMENTAL

- **Materials**

1. Pyrrole (reagent grade) is distilled prior to use.
2. Ammonium per sulphate, emulsion grade Polyvinyl chloride, cyclohexanone are used as received.

- **Preparation**

1. *polypyrrole*

Chemical oxidative polymerization of pyrrole is carried out using ammonium per sulphate as initiator[42] in the presence of 1M HCl. The polymerization is carried out for 4 hrs. at room temperature. It is then filtered, washed and dried under different conditions like room temperature (48 hrs.), in oven (at 50-60°C for 6 hrs.), in vacuum (at room temperature, for 16 hrs.). The dielectric properties of the all samples are studied using cavity perturbation technique.

2. *Preparation of PPy/PVC SIPN in pellet form*

Chemical oxidative polymerization of pyrrole / polyvinyl chloride SIPN is also prepared as given above. Different proportions like 1:1,1:1.5,1:2,1:2.5 are prepared, the samples are pelletized and the dielectric properties are measured at S band(2-4 GHz).

3. *Preparation of cyclohexanone soluble PPy/PVC SIPN*

Polypyrrole / Polyvinyl chloride (PPY/PVC) SIPN in soluble form is prepared by the chemical oxidative polymerization of pyrrole using ammonium per sulphate as initiator in the presence of emulsion grade polyvinyl chloride solution in cyclohexanone. It is then made in to film by solution casting and is doped with 1M HCl. Different compositions of PAN-PVC SIPN's, say2:1,1:1,1:2,1:3 are prepared. It is very difficult to prepare the film of SIPN's of 2:1and 1:1 PPy :PVC compositions. Therefore the dielectric properties of SIPN's from 1:2 composition is studied. Cavities operating at S, C and X bands are used for the study.

5.3.2 RESULTS AND DISCUSSION

(a) Characterization

Figure 5.10 and 5.11 shows the IR spectra of polypyrrole prepared using ferric chloride as the initiator (PPy I) and ammonium per sulphate as the initiator (PPy II) respectively. In both figures the characteristic peaks around 600 cm^{-1} due to the presence of halogens, at 920 cm^{-1}, 1046 cm^{-1}, 1192 cm^{-1}, 1461 cm^{-1} and 1650 cm^{-1} due to the presence of conducting polypyrrole are same.

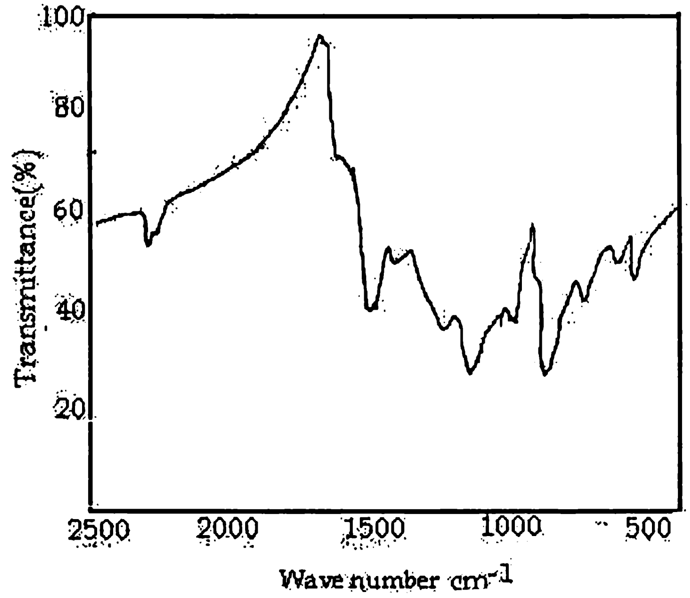


Fig.5.10: IR spectrum of PPy (I).

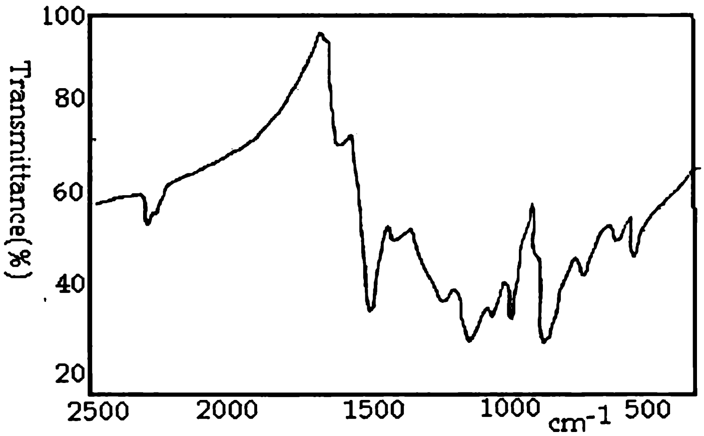


Fig.5.11: IR spectrum of PPy [$(NH_4)_2S_2O_8$].

(b) Effect of different drying conditions on dielectric properties

Figure 5.12 shows the variation of conductivity and figure 5.13 shows the variation of dielectric heating coefficient of polypyrrole at different drying conditions. The figure 5.12 shows that the conductivity is higher for oven dried sample as in the case of polyaniline and poly o-toluidine. Also figure 5.13indicates that the dielectric heating coefficient is minimum for oven dried sample.

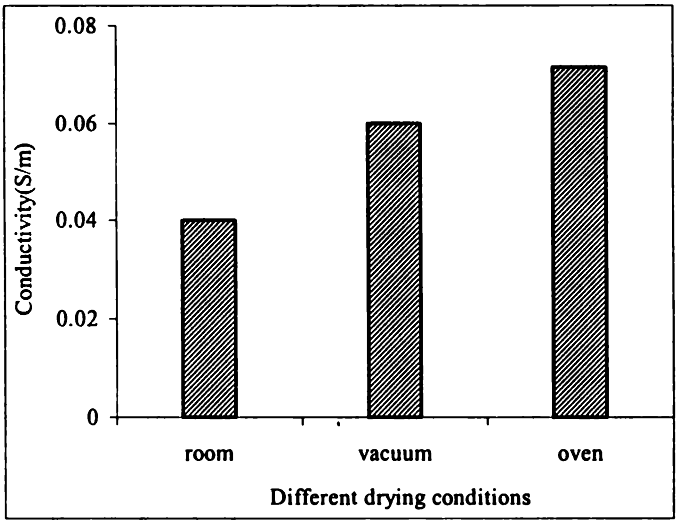


Fig 5.12: Variation of conductivity of polypyrrole with drying conditions at 2.97GHz.

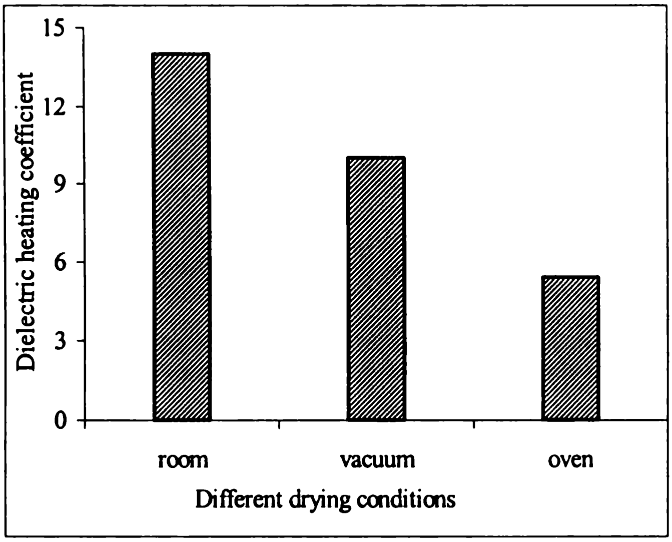


Fig 5.13: Variation of dielectric heating coefficient with drying conditions at 2.97 GHz.

(c) Variation of dielectric properties with compositions

1. Dielectric loss and conductivity

Figure 5.14 shows the dielectric loss and conductivity of different compositions of PPy: PVC SIPN. It is clear from the figure that the dielectric loss and conductivity increases with increase in PVC content and it reaches a maximum at 1:2 proportion and then it decreases as in the case of SIPN prepared using ferric chloride as the initiator.

2. Dielectric heating coefficient(J)

It is clear from the figure 5.15 that the dielectric heating coefficient is minimum for 1:2 composition. This composition is suitable for dielectric heating applications.

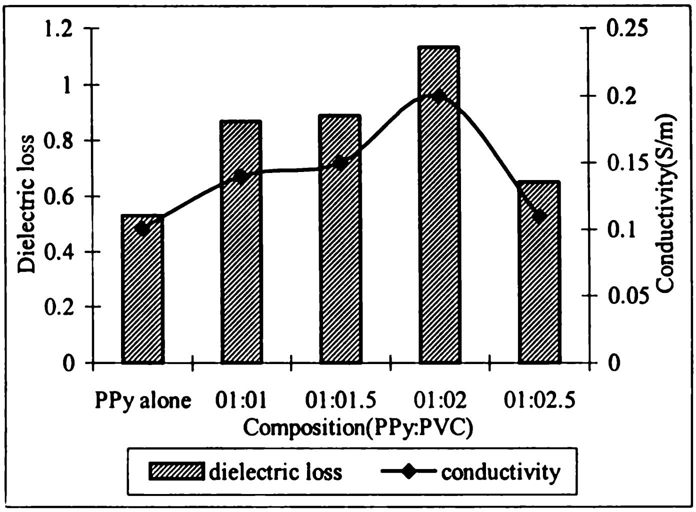


Fig 5.14: Variation of dielectric loss and conductivity of PPy :PVC SIPN's with compositions at 2.97 GHz.

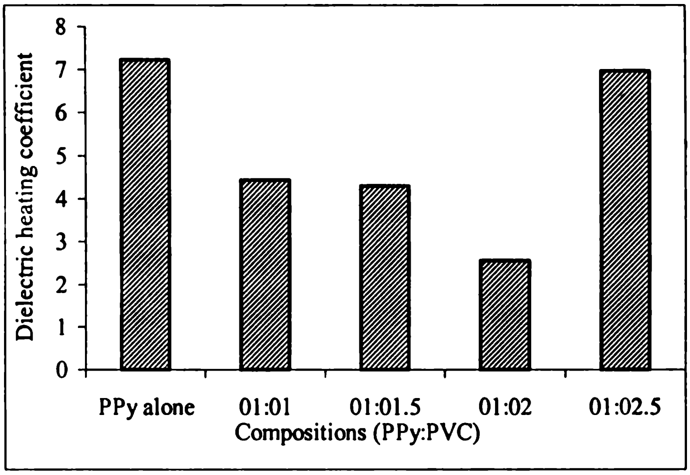


Fig 5.15: Variation of dielectric heating coefficient of PPy :PVC SIPN with compositions at 2.97 GHz.

3. Absorption coefficient and skin depth.

Figure 5.16 shows the variation of absorption coefficient and the skin depth of different compositions of SIPN. Since the absorption coefficient is directly related to the dielectric loss factor the absorption coefficient is higher for 1:2 composition. The skin depth is least for 1:2 composition.

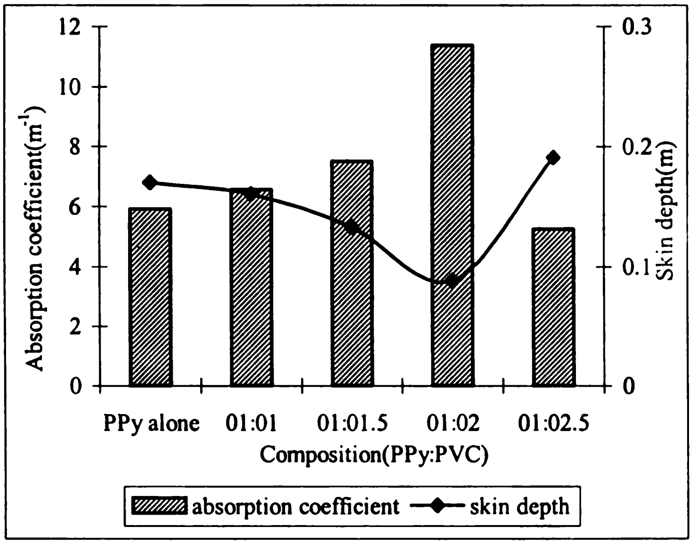


Figure 5.16: Variation of absorption coefficient and skin depth of PPy:PVC SIPN with compositions at 2.97 GHz.

From all these properties the 1:2 Pani:PVC composition is optimized.

(d) Variation of dielectric properties with frequency

1. Dielectric loss and conductivity

Figure 5.17 shows the variation of dielectric loss of oven-dried polypyrrole and PPy: PVC (1:2) SIPN. The dielectric loss increases with increase in frequency due to the frictional loss at higher frequencies. Since the conductivity is directly related to the dielectric loss factor, the variation of conductivity of both samples with frequency is same as that of dielectric loss with frequency (figure 5.18).

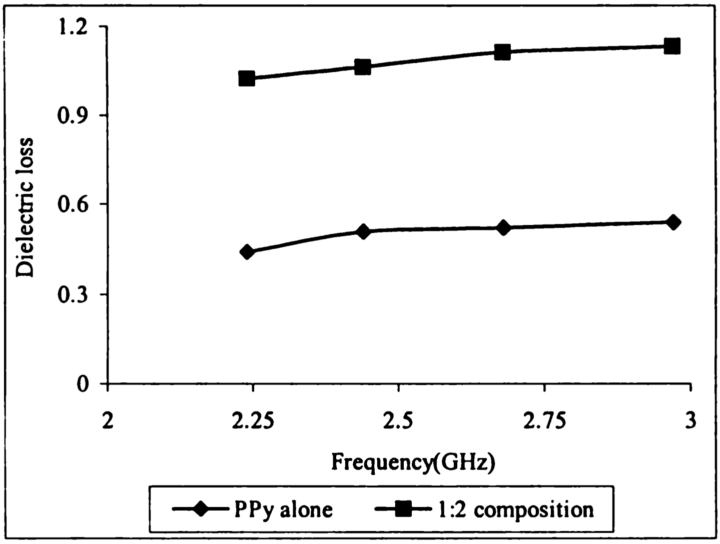


Fig 5.17: Variation of dielectric loss of with frequency

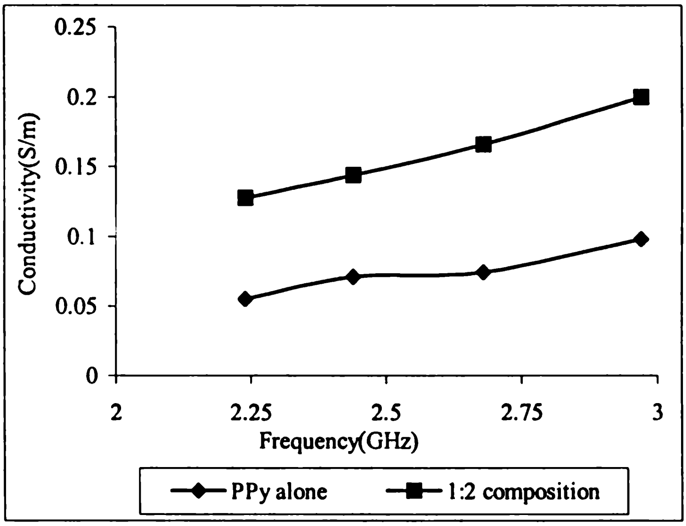


Fig 5.18: Variation of conductivity with frequency.

2. Dielectric constant

Dielectric constant decreases with increase in frequency in both cases, as shown in figure 5.19. At higher frequencies, due to the frictional loss caused by the rotational displacement of molecular dipoles under the influence of alternating field increases the dielectric loss and this might results in a decrease in dielectric constant.

3. Dielectric heating coefficient

Dielectric heating coefficient decreases with increase in frequency (figure 5.21). The heating property is inversely related to the dielectric loss factor and there fore at higher frequencies the heating coefficient is decreased. The lower the heating coefficient, the better will be the material for heating applications.

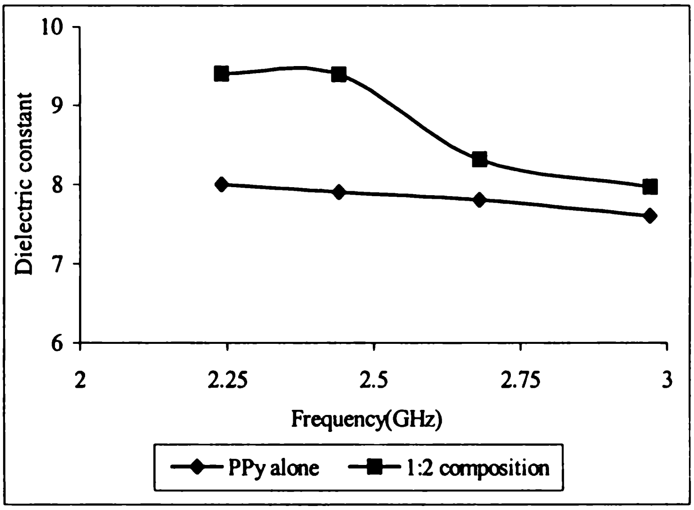


Fig 5.19: Variation of dielectric constant with frequency.

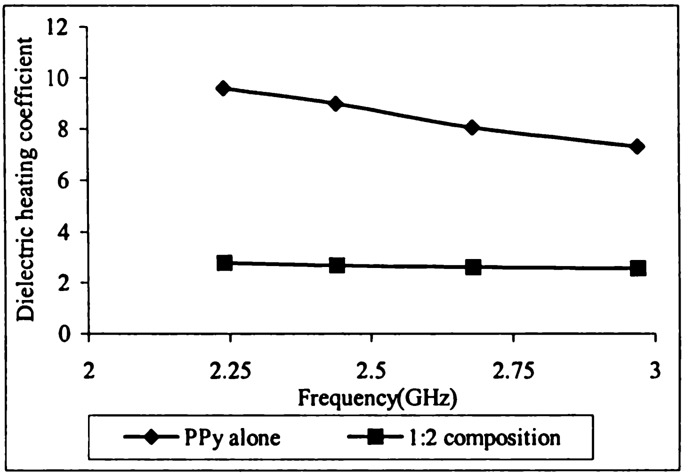


Fig 5.20: Variation of dielectric heating coefficient with frequency.

4. Loss tangent

The loss tangent or dielectric loss angle is directly related to dielectric loss factor and therefore it shows the same behaviour as that of dielectric loss. The loss tangent increases with increase in frequency as shown in figure 5.21.

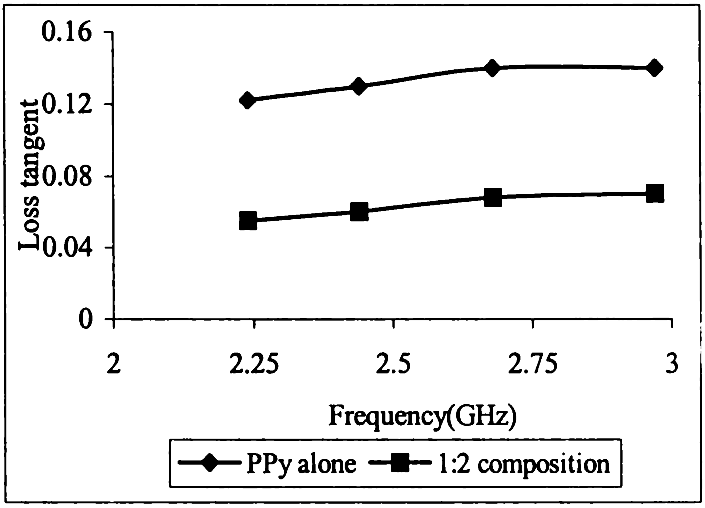


Fig 5.21: Variation of loss tangent with frequency.

5. Absorption coefficient and skin depth

Figures 5.22and 5.23 show the variation of absorption coefficient and skin depth of polypyrrole and 1:2 composition with frequency. The figures show that the absorption coefficient increases with increase in frequency and the skin depth decreases with increase in frequency. It is also clear from the figures that the SIPN shows high absorption coefficient and low skin depth when compared to polypyrrole.

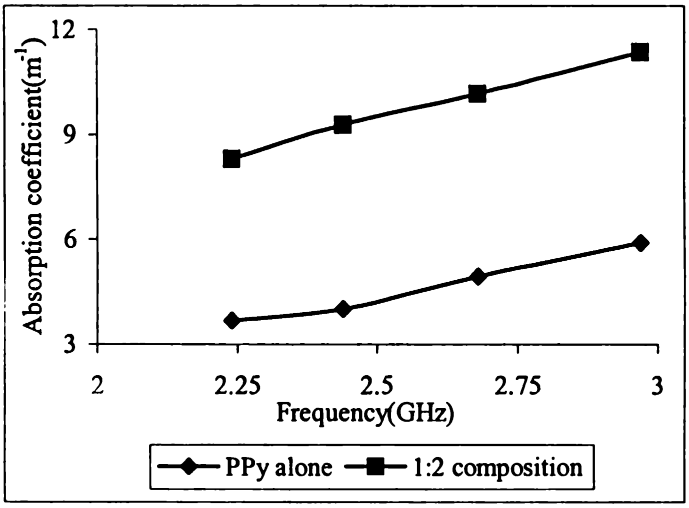


Fig 5.22: Variation of absorption coefficient with frequency.

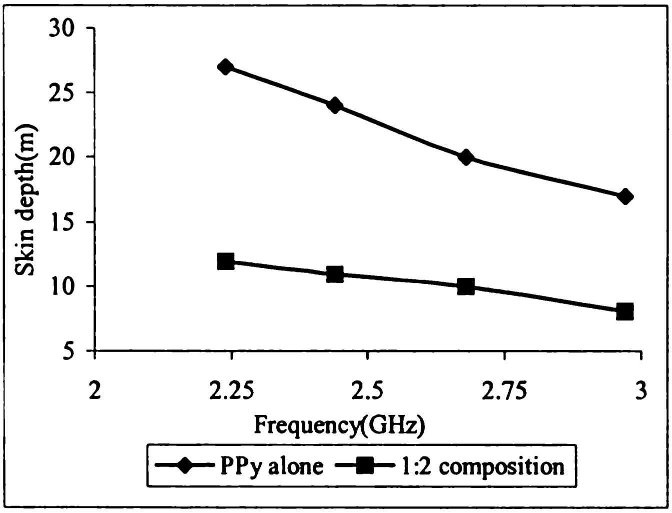


Fig.5. 23: Variation of skin depth with frequency.

(e) DSC and TGA studies.

Figure 5.24 shows the DSC thermogram of polypyrrole and its SIPN of 1:2 (PPy:PVC) composition. It is clear from the figure that the glass transition temperature (Tg) of PPy in the SIPN is shifted to 113°C from 120°C of PPy. The lower Tg shift is due to the presence of PVC, which makes the polypyrrole chains more flexible due to its plasticizing action.

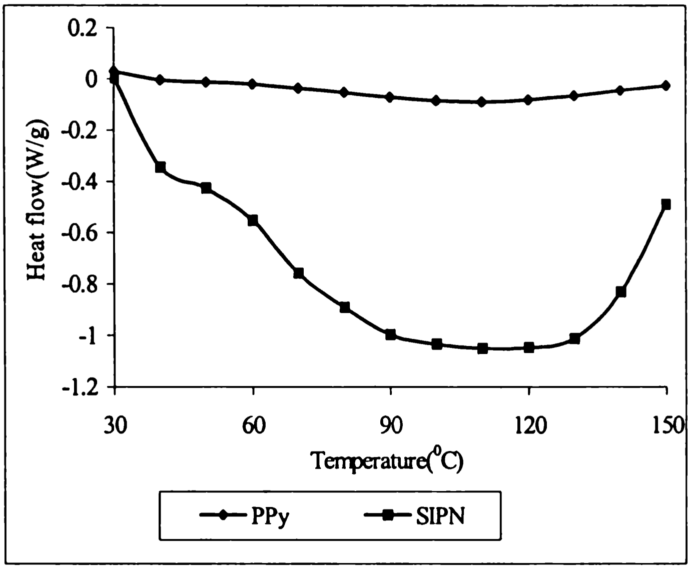


Fig.5.24: DSC of PPy and PPy:PVC SIPN

Figure 5.25 shows the TGA thermogram of PPy and its SIPN of 1:2 (PPy:PVC). It is clear from the figure that the initial loss of SIPN is 9% at 280 °C and that in the case of PPy is 25% . The initial loss of SIPN is reduced due to the presence of PVC. But the second loss in the case of SIPN, due to the degradation of PVC, is higher (44% at 390 ºC) compared to PPy alone (38% at 390 ºC). A residue of 12 % for PPy and 10% for the SIPN is obtained.

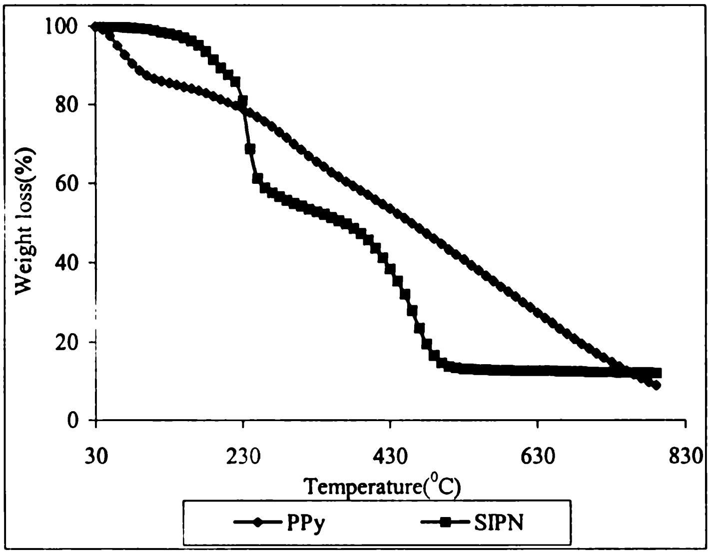


Fig.5.25: TGA thermogram of PPy and PPy:PVC(1:2)SIPN.

(f) LOW FREQUENCY STUDIES

Figure 5.26 shows the conductivity of polypyrrole alone and its SIPN of 1:2 (PPy :PVC) composition at lower frequencies (10 Hz to 10 MHz). It is clear from the figure that polypyrrole shows higher conductivity at lower frequencies than that of SIPN , as in the case of polyaniline.

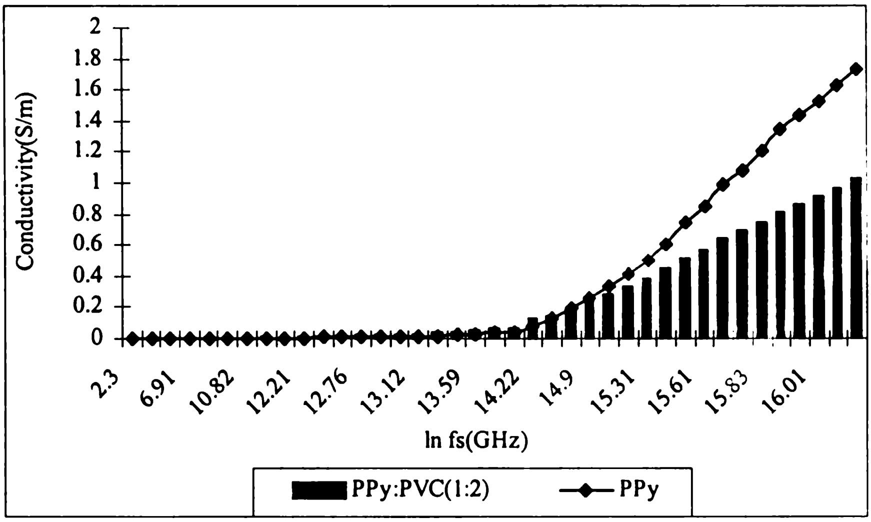


Fig.5.26: Conductivity of polypyrrole and its SIPN at lower frequencies.

(g) SEM Analysis

Figures 5.27,5.28 and 5.29 shows the scanning electron micrographs of PPy, PVC and PPy:PVC SIPN of 1:2 composition. Figure 5.27 shows that the polypyrrole chains are loosely packed. In the case of SIPN (figure 5.29) there is no separate domains for PPy and PVC and it shows that the PPy chains are interpenetrated into the PVC (globular shaped as shown in figure 5.28). It attains an interpenetrated network structure as in the case of polyaniline.

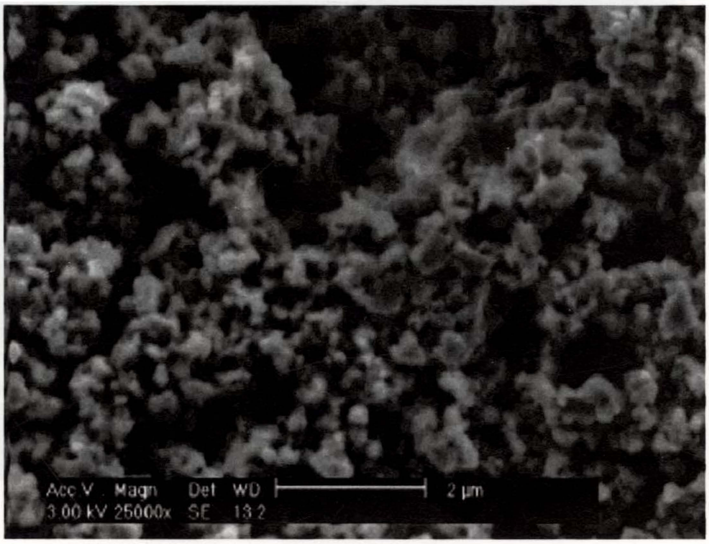


Fig.5.27: SEM micrograph of PPy alone.

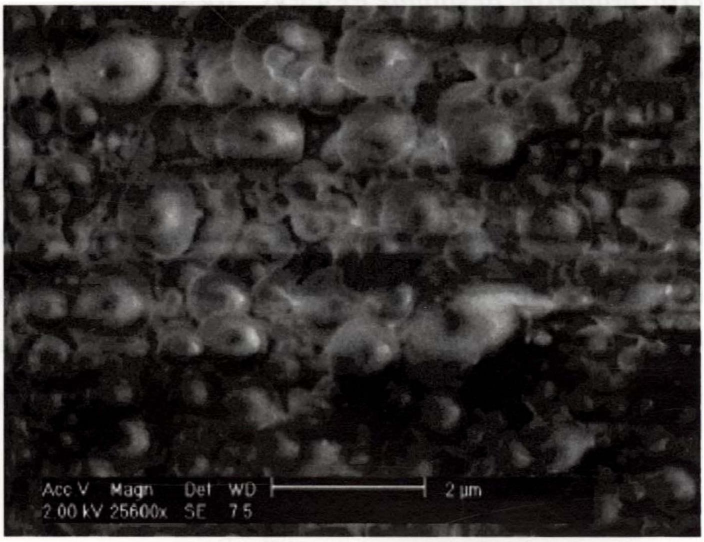


Fig.5.28: SEM micrograph of PVC alone.

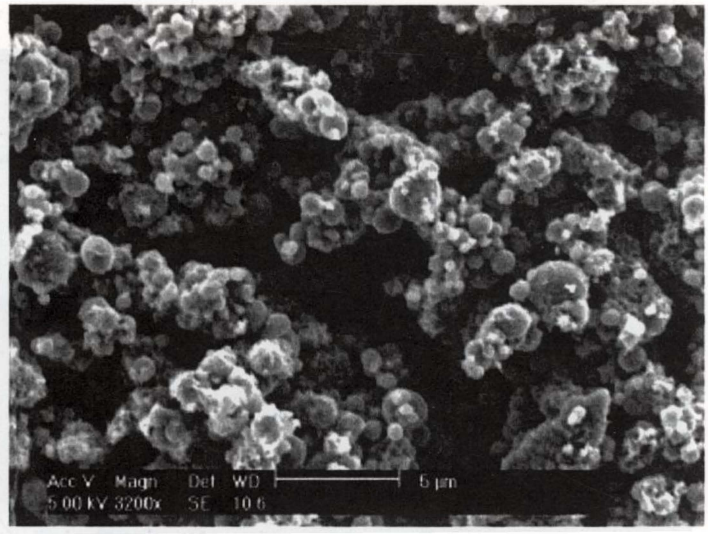


Fig.5.29: SEM micrograph of PPy:PVC SIPN.

5.4. Dielectric properties of soluble PPy:PVC SIPN

(a) Dielectric properties of SIPN's at different bands.

Table 5.2 shows the dielectric properties of SIPN at different bands. It is clear from the table that the loss and the conductivity are higher at S. Compared to C band, X band shows higher values for dielectric loss and conductivity. At very high frequencies the frictional loss contribute a high dielectric loss and conductivity. Also the dielectric constant and absorption coefficient are higher for S band when compared to C and X bands. The dielectric heating coefficient and skin depth are lower for S band.

Table 5.2: Dielectric properties of SIPN's at S, C and X bands

Frequency (GHz)	Properties					
	E"	σ(S/m)	ε'	$\alpha_{(f)}(m^{-1})$	$\delta_{(f)}$(m)	J
2.97(S band)	2.72	.6	8	27.6	.04	.63
7.64(C band)	0.225	0.1	2.9	10.5	.10	16.09
11.84(X band)	0.41	0.27	3.43	27.62	.04	6.96

Therefore the dielectric properties at the S band is selected for further studies.

(b) Variation of dielectric properties with frequency

1. Dielectric loss and conductivity

Figure 5.30 shows that the variation of the imaginary part of the complex permittivity or the dielectric loss factor ε''_r of different proportions of SIPN's with frequency. The dielectric loss is found to increase with frequency with a slight dip in the middle frequencies. This is in agreement with the pellet form of SIPN. Figure 5.31 indicates that the conductivity also shows the same behaviour as dielectric loss.

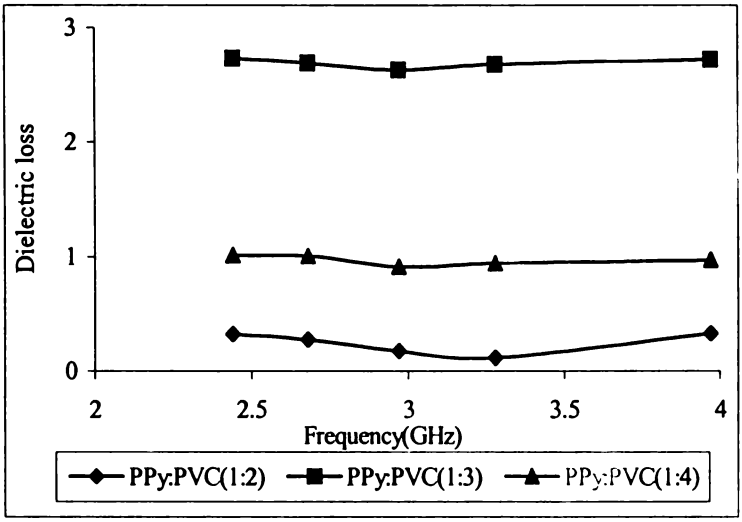


Fig 5.30: Variation of dielectric loss with frequency.

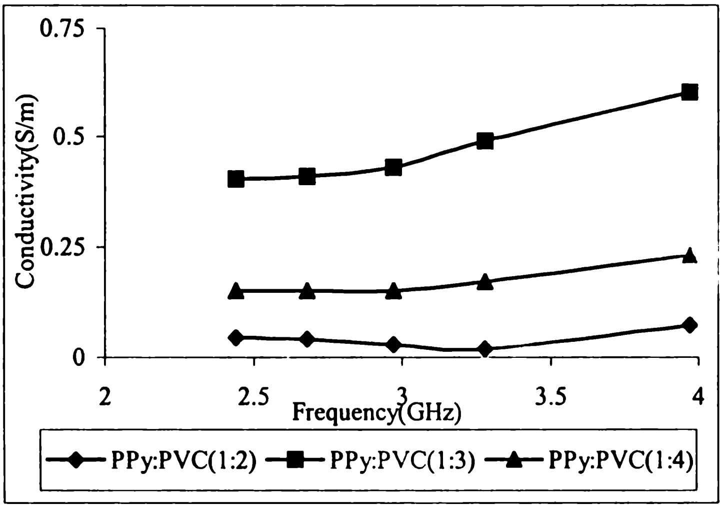


Fig 5.31: Variation of conductivity with frequency.

2. Dielectric constant

The real part of complex permittivity (dielectric constant) of different compositions of the SIPN's decrease with increase in frequency as shown in figure 5.32. At higher frequency, the orientation polarization-takes place and this lead to a high dielectric loss and this results in decrease of dielectric constant as in the case of polyaniline.

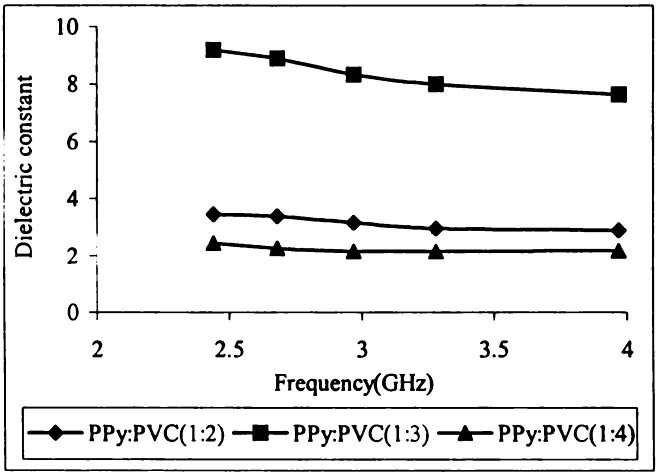


Fig 5.32: Variation of dielectric constant with frequency

3. Loss tangent

Figure 5.33 shows the variation of loss tangent for different proportions with frequency. The tanδ is directly related to the dielectric loss factor and it also shows the same behaviour as that of dielectric loss.

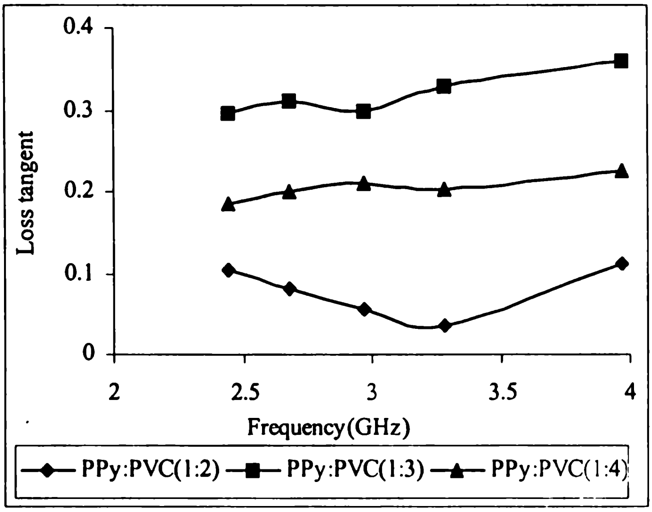


Fig 5.33: Variation of loss tangent with frequency

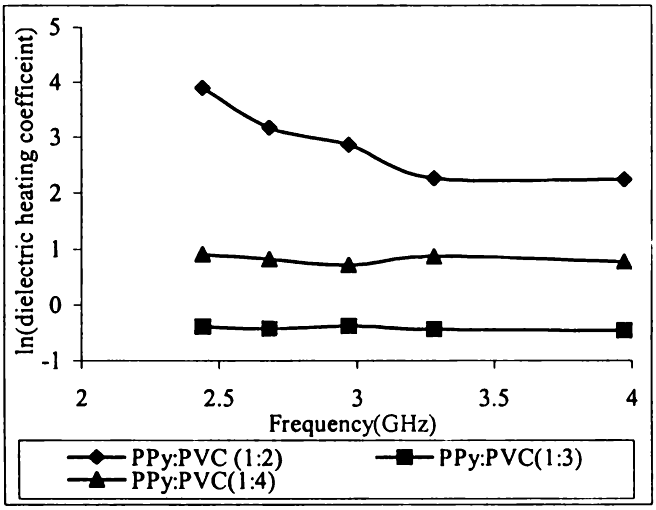


Fig 5.34: Variation of heating coefficient with frequency

4. Dielectric heating coefficient(J)

Figure 5.34 shows the variation of dielectric heating coefficient of different SIPN's with frequency. It is observed that the heating property increases with increase in frequency. It is clear from the figure that the dielectric heating coefficient is less at higher frequency.

(c) Variation of dielectric properties with compositions.

Figure 5.35 shows the variation of dielectric loss and conductivity with different compositions. It is observed that the dielectric loss and conductivity increases with increase in PVC content up to 1:3 (PPy: PVC) proportion and then it decreases. It is due to the interfacial polarization in the presence of weakly polar PVC as expected. The quantity and geometry of the PVC at 1:3 proportion is more favourable for the high dielectric loss and conductivity.

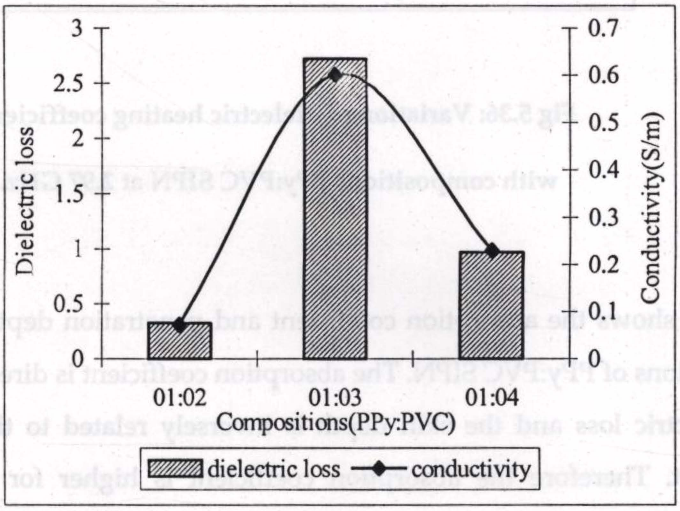


Fig.5.35: Variation of dielectric loss and conductivity with composition of PPy:PVC at 2.97 GHz.

The dielectric heating coefficient is found to be lower for 1:3 (PPy : PVC) composition as shown in figure 5.36. When the dielectric loss increases the dielectric heating coefficient decreases. Since the dielectric loss of 1:3 composition is high, the heating coefficient is low at that composition.

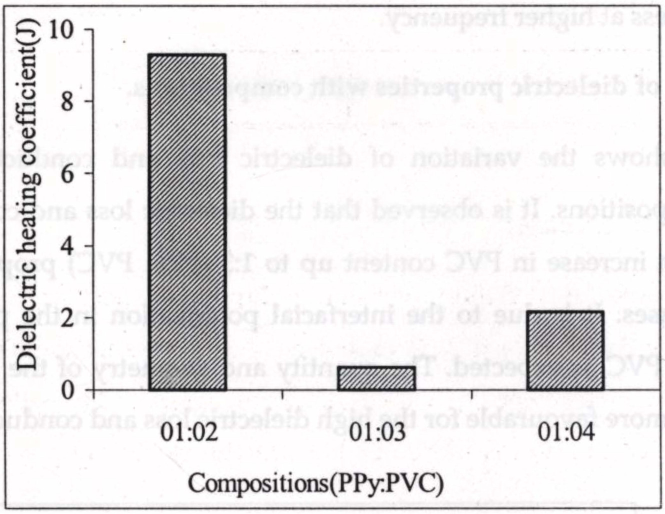


Fig 5.36: Variation of dielectric heating coefficient with compositions PPy:PVC SIPN at 2.97 GHz.

Table 5.3 shows the absorption coefficient and penetration depth of different compositions of PPy:PVC SIPN. The absorption coefficient is directly related to the dielectric loss and the skin depth is inversely related to the absorption coefficient. Therefore the absorption coefficient is higher for 1:3 PPy:PVC composition and the skin depth is minimum for that composition as shown in table 5.3.

Table 5.3: Absorption coefficient and skin depth of SIPN's at 2.97 GHz

	Composition(PPy :PVC)		
	1:2	1:3	1:4
Absorption coefficient(m^{-1})	4.5	27.61	22
Skin depth(m)	.22	.04	.07

(d) TGA and DSC studies

Figure 5.37 shows the DSC thermogram of polypyrrole and PPy :PVC SIPN of 1:3 composition in film form. It is clear from he figure that the Tg of PPy is shifted to 109 ^{0}C. The lower Tg value of film form compared to pellet form (113 ^{0}C) indicates that the film is more flexible and this flexibility gives a positive response to the microwave conductivity. The Tg is lowered due to the plastizing action of the polyvinyl chloride.

Figure 5.38 shows the TGA of PPy and SIPN. The figure indicates that there is an initial loss of 20% at 230 ^{0}C and a second loss of 18% at 380 ^{0}C for PPy. In the case of SIPN an initial loss of 16% and a second loss of 37% is observed. The initial loss is reduced in the case of SIPN is due to the presence of PVC as explained earlier. The second loss of the SIPN is high due to the degradation of PVC.

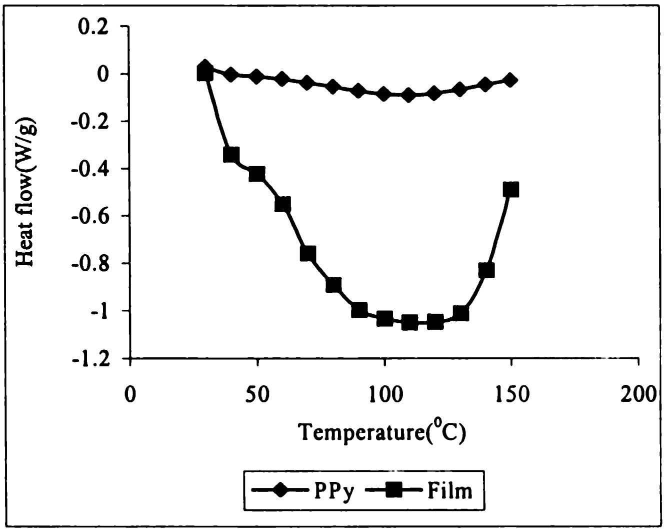


Fig.5.37 : DSC of PPy and SIPN in film form.

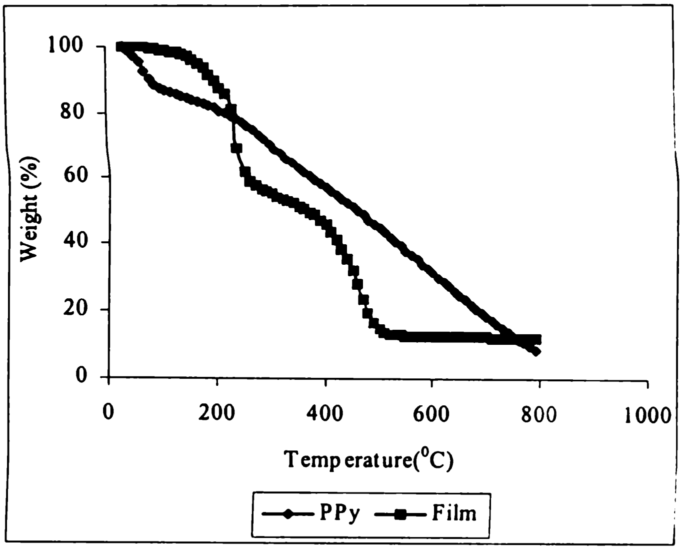


Fig.5.38 : TGA of PPy and SIPN of film form

5.5 Comparison of Polypyrrole and Its SIPN's

(a) Comparison of polypyrrole prepared by two methods

The comparison of polypyrrole prepared by two methods is very essential so that we could select a particular method for the microwave frequencies.

The conductivity of both polypyrrole samples is shown in table 5.4. The table shows that the conductivity is very high, i.e., of the order of 10 times, for polypyrrole prepared using ammonium per sulfate as the initiator (II) compared to that prepared using ferric chloride initiator (PPyI). The microwave conductivity is directly related to the dopant concentration and the dopant concentration in the case of polypyrrole prepared by using ammonium per sulfate is higher because the reaction is done in the presence of excess HCl. The yield of polypyrrole prepared by this method is double when compared to that of polypyrrole prepared by using ferric chloride as the initiator.

Table 5.4: Dielectric properties of PPy I and PPy II at 2.97 GHz.

	PPy I	PPy II
σ (S/m)	0.02	0.12
$\varepsilon'r$	2.6	2.97
lnJ	1.2	2
$\alpha_f(m^{-1})$	2.46	5.9
$\delta_f(m)$	.41	.17

The dielectric constant is higher for polypyrrole prepared by using ammonium persulfate as the initiator. The dielectric constant is higher due to the accumulation of more polar groups in this case. The absorption coefficient is high and the skin depth is low for the polypyrrole prepared by this method.

The dielectric heating coefficient is less for polypyrrole and the SIPN prepared using ferric chloride as the initiator. The conductivity of PPy: PVC SIPN prepared by both methods shows comparable values. In the case of SIPN the presence of PVC leads to interfacial polarisation and this polarisation may be same in both cases. So the conductivity values show comparable result.

Figure 5.39 shows the DSC thermogram of PPy I and PPy II. It is clear from the figure that the Tg of PPy I is at 152^{0}C and at 120^{0}C for PPy II. The lower Tg of PPy II indicates that the chain is more flexible than PPy I, which will contribute a higher conductivity in the microwave frequencies.

Figure 5.40 shows the TGA thermogram of two polypyrroles. It is clear from the figure that an initial loss of 10 % in the case of PPy I and 22 % weight loss in the case of PPy II up to 260 ^{0}C. The initial loss is due to the volatilization of dopant molecules and the higher percentage of weight loss in the case of PPy II is due to the higher dopant concentration. The second loss i.e., from 260 ^{0}C to 420 ^{0}C a weight loss of 45 % in PPy I and 25 % in PPy II is observed. It indicates that the polypyrrole prepared using ammonium persulfate as the initiator is more stable than that prepared using ferric chloride. Also a residue of 23 % in the case of PPy I and 9 % in the case of PPy II is observed.

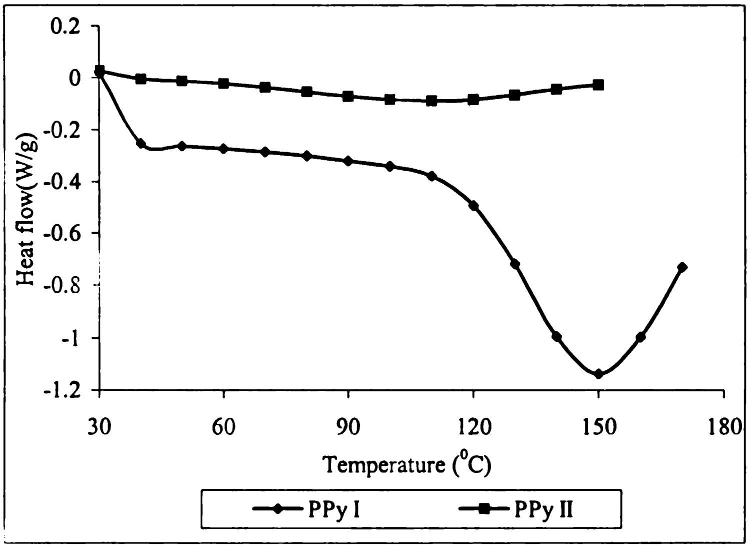


Fig.5.39: DSC thermogram of PPy I and PPy II

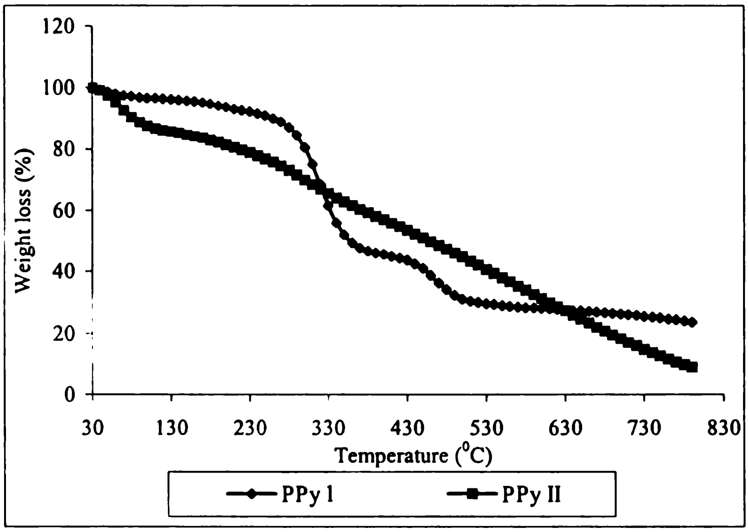


Fig. 5.40: TGA thermogram of PPy I and PPy II

(b) Comparison of SPIN's of PPy I and PPy II in pellet form.

Table 5.5 shows the dielectric properties of SIPN's of PPy I and PPy II. It also shows the same trend as that of PPy alone.

Table 5.5: Dielectric properties of SIPN's of PPy I and PPy II

	PPy I :PVC SIPN(1:2)	PPy II:PVC SIPN(1:2)
σ (S/m)	0.152	0.2
$\varepsilon'r$	5.4	7.96
lnJ	0.35	0.9
$\alpha_f(m^{-1})$	13.05	11.36
$\delta_f(m)$	0.08	0.09

(c) Comparison of pellet and film form of PPy:PVC prepared by using ammonium persulfate as the initiator

Table 5.6 shows the dielectric properties of SIPN's of pellet (1:2 PPy:PVC composition) and film (1:3 which shows better results than 1:2 film) forms. It is clear from the table that the conductivity and absorption coefficient are higher for film sample. Also the dielectric heating coefficient and skin depth are lower for the film samples. The reason is same as explained earlier.

Table 5.5: **Dielectric properties of SIPN's in pellet and film forms**

	1:2 (PPy :PVC)	1:3(PPy :PVC)
σ (S/m)	0.2	0.602
J	2.56	0.63
$\alpha_f(m^{-1})$	11.36	38.97
$\delta_f(m)$	0.09	0 .03

5.6. CONCLUSIONS

- Dielectric properties of polypyrrole prepared by two methods are depended on frequency.
- The conductivity and dielectric constant of polypyrrole prepared using ammonium persulfate is higher compared to that of ferric chloride initiated synthesis.
- The yield is high for ammonium per sulfate initiated polymerization.
- The absorption coefficient is high and the skin depth is low for PPy prepared using ammonium persulfate initiator.
- The conductivity and the dielectric constant of SIPN's prepared using ammonium persulfate initiator shows higher value.
- The dielectric heating coefficient of SIPN prepared in pellet form using ferric chloride initiator shows lower value and is more apt for dielectric heating applications.
- The film form of SIPN is superior to pellet form in terms of conductivity, heating coefficient, absorption coefficient and skin depth.
- The dielectric loss and conductivity are higher for 1:2 PPy:PVC composition in pellet form(for PPy I and PPy II) and 1:3 composition in film form.
- The dielectric heating coefficient is minimum for 1:2 composition for pellet samples and 1:3 composition for film samples.
- The dielectric properties at S band is better than that of C and X bands in the case of film SIPN's.
- The absorption coefficient of 1:2 composition for pellet samples and 1:3 composition for film samples are high.
- The skin depth of 1:2 composition for pellet samples and 1:3 composition for film samples are less.

5.7 REFERENCES

1. J.C.Vidal, E.Garcia, J.R.Castillo, *Anal.Chim. Acta,* **385**,213(1999).
2. T.E.Cambell, A.J.Hodgason, G.G.Wallace, *Electroanalysis* **11**,215,(1999).
3. D.Kineal,A.Kamer, A.D.Child, J.R.Reynold, *Synth.Metals,* **92**,53,(1998).
4. N.T.Kemb, G.U.Flanagan, A.B.Kaiser, H.J.Trodahl, B.Chapman, A.C.Patridge, R.G.Buckley, *Synth.Metals,***101**,434,(1999).
5. C.Jerome, D.Labaye, I.Bodart, R.Jerome, *Synth.Metals,* **101**,3,(1999).
6. E.Smela, J.Micromech, *Microeng.,***9**,1,(1999).
7. S.C.yang, H.Liu, R.L.Clark, *PCT Int.Appl.* WO 99,**22**,380(Cl.H01 Bl/00).
8. T.Takamatsu,Y. taketani, *Jpn.Kokai,Tokyo Koho JP 11* **121**,279,(1999).
9. Y.Kojima, H.Kamikawa, T. Takamatsu, *Jpn.Kokai.Tokyo Koho JP11* **121**, 280 (1999).
10. T.A.skotheim, R.Elsenbaumer, J.reynolds (Edn.), *Handbook of Conducting polymers,* Marcel Dekker, New York, (1986).
11. T.A.skotheim, R.Elsenbaumer, J.reynolds (Edn.), *Handbook of Conducting polymers,* Marcel Dekker, New York, (1998).
12. G.G.Wallace, G.Spinks, P.R.Teasdate, *Conductive Electroactive Polymers, Technomic,* New York, (1997).
13. J.O.Iroh, C.Williams, *Synth.Metals,* **99**,1,(1999).
14. W.Su.J.O.Iroh, *Synth.Metals,* **95**,159,(1998).
15. A.B.smith, C.J.Knowles, *J.Appl.Poly.Sci.,* **43**,399,(1991).

16. M.Biswas, A.Roy, *J.Appl.Poly.Sci.*,**51**,1575,(1994).
17. Y.Lu, G.Shi, C.Li, Y.Liang, *J.Appl.Poly.Sci.*, **70**,2169,(1998).
18. T.Silk, H.Qi, J.Tamm., R.G.Compton, *Synth.Metals*, **93**,59,(1998).
19. T.Silk, H.Qi, J.Tamm, R.G.Compton, *Synth.Metals*, **93**,65,(1998).
20. R.ansari, G.G.Wallace, *Polymer*, **35**,2372,(1994).
21. R.Singh, A.K.Narula, R.P. Tandon, S.U.M. Rao, V.S.Panwar, A.mansingh, S.Chandra, *Synth.Metals*, **79**,1,(1996).
22. M.Saeak, U.Akbulut, D.N.Batchelarer, *Polymer*, **39**,4735,(1998).
23. H.Zhao, W.L.Price, G.G.Wallace, *J.Member.Sci.*, **148**,161,(1998).
24. M.Morita, *J.Appl.Poly.Sci.*, **70**,647,(1998).
25. M.Nikpour, H.Ghaouk, A.Mau, D.J.Chung, G.Wallace, *Synth.Metals*, **99**,121,(1999).
26. P.Audebert, P.Aldebert, N.Grirault, *Synth.Metals*, 58,259,(1993).
27. M.Biswas, A.Roy, *J. Appl.Poly.Sci.*, **49**,2189,(1993).
28. E.Rubenstein, J.S.Park, *J. Appl.Poly.Sci*, **42**,925, (1991).
29. J.M.Davey, S.F.Ralph, C.O.Too, G.G.wallace, *Synth.Metals*, **99**,191, (1999).
30. M.Makhlouki, M.Morsli, A.Bonnet, A.Conana, S.Lefrant, *J. Appl.Poly.Sci*, **4**,443, (1992).
31. S.Marchant, F.R.Jones, T.P.C.Wong, P.V.Wright, *Synth.Metals*, **96**,35, (1998).
32. M.Chakraborty, D.C.Mukherjee, B.M.Mandal, *Synth.Metals*, **98**,193, (1998).
33. Al.Nazzal, G.B.Street, *J.Chem.Soci. Chem.Commun.*, 375(1985).

34. B.Tieke and W. Gabriel, *Polymer,* 31,20,(1990)

35. T.Kunugi,H.Okazaki, *Jpn.Kokai Tokyo Koho JPII* 159,**443**,(99,159,443).

36. H. S. O. Chan, H. Hopok, E. Khor.and M. M. Tan., *Synth.Met.,* **31**, 95, (1995)

37. M. A. De Paoli, R.J.Waltman, A. F. Diaz and J. Bargon, *J. Chem. Soc., Chem.commun.,* 1015,(1984)

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

39. M. Makhlouki, M. Morsli, A.Bonnet, A. Conan, A.Pron and S. Lefrant, *J. Appl. Polym.* Sci., **44**,443,(1992)

40. T. K. Mandal and B. M. Mandal, *Synth. Metal,* **80**,83, (1996)

41. S.machida, S.Miyata, A.Techagumpuch, *Synth.Metals,* **31**,31,(1989).

42. Y.Liu, G.Shi, C.Li.Y.Liang, *J.Appl.Poly.Sci.,* 70,2169,(1998).

Chapter 6

COMPARATIVE AND APPLICATIONS STUDY

PART 1

6.1 A COMPARATIVE STUDY

Conjugated polymers in the undoped and doped states have an array of potential applications in the microelectronic industry. They have been proved to be excellent replacement for metals and semiconductors in electrochemical applications notably for energy storage, corrosion protection, electrochromic devices, electrochemical sensors etc. They have recently attracted significant attention from all polymer branches with growing interdisciplinary trend. Stability, processing characteristics, low cost and lightweight are its interesting features. Considering the applications of conducting polymers especially in EMI shielding, microwave filters, radar, satellite communication systems etc it is very relevant to study the dielectric properties in the microwave frequencies. Among the conductive composites studied in this thesis, the semi inter penetrating networks with polyvinyl chloride is found to be important in microwave applications.

In this chapter we report a comparative study on the dielectric properties of selected conducting polymers like polyaniline, polypyrrole and poly o-toluidine and its SIPN's with polyvinyl chloride. Various properties like dielectric constant, dielectric loss, conductivity, heating coefficient, absorption coefficient and skin depth are compared. These comparisons will help us to select a particular polymer for a specific application. Some preliminary studies on certain applications of conducting polymers are also included in this thesis.

♦ *Preparation*

Conducting polyaniline and its SIPN in different forms are prepared as explained in chapter 3. The preparation of poly o-toluidine and its SIPN in different forms are same as explained in chapter 4. Preparation of poly pyrrole using ferric chloride as the initiator (PPy I), preparation of polypyrrole using ammonium persulfate initiator (PPy II) and its SIPN's with PVC are same as explained in chapter5.

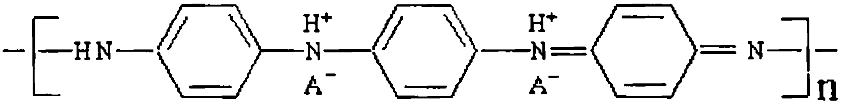
The frequencies of 2.97 GHz (S band), 7.56 GHz(C band), and 11.98 GHz (X band) are selected for the comparative study. Among the conductive composites Pani: PVC SIPN of 1:1.5(pellet and film), POT: PVC of 1: 3(pellet and film), PPy: PVC of 1:2 (prepared by two methods in pellet form) and PPy :PVC SIPN of 1:3(film form, prepared using ammonium per sulfate) compositions are selected because of the superior properties of these compositions.

6.1.2 RESULTS AND DISCUSSION

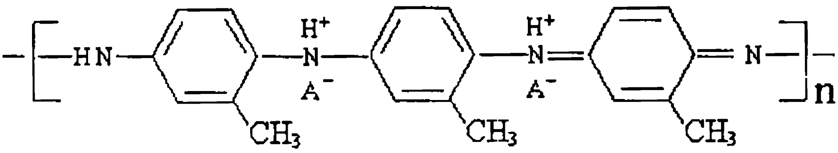
(a) Pellet samples

1. Dielectric loss ($\varepsilon''r$) and conductivity(σ)

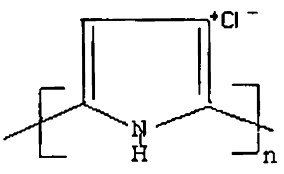
Figures 6.1 and 6.2 show the dielectric loss and conductivity of conducting polymers and of conducting semi inter penetrating networks respectively. It is clear from the figure 6.1 that the polyaniline has the highest dielectric loss and conductivity compared to poly o-toluidine and polypyrrole. The dielectric loss is due to the dielectric relaxation process resulting from the rotational displacement of polar groups in an a.c. field. The dipolar polarisation is higher for polyaniline due to its favorable structure of polyaniline.



STUCTURE OF CONDUCTING POLYANILINE



STRUCTURE OF CONDUCTING POLY O-TOLUIDINE



STRUCTURE OF CONDUCTING POLYPYRROLE

Analyzing the structures of poly aniline, poly o-toluidine and polypyrrole it is evident that the dipole developed in polyaniline due to the protonation, i.e.,-NH^+Cl^- 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 a sterric hindrance and it may adversely affect the easy dipole change in poly *o*-toluidine. In the case of polypyrrole, the rotational displacement of -NH^+Cl^- is more restricted because of the presence of the -NH group on the ring itself. The microwave conductivity is also shows the same nature of variation as that of dielectric loss factor.

When the weakly polar PVC is added the interfacial polarisation-takes place and leading to dielectric loss. It is clear from the figure 6.2 that the dielectric loss and conductivity are in the order Pani: PVC > PPy II: PVC > POT: PVC > PPy I: PVC. In the case of poly o-toluidine the CH_3 group pushes PVC apart from the chain and this lead to a decrease in interfacial polarisation compared to polypyrrole prepared using ammonium per sulfate.

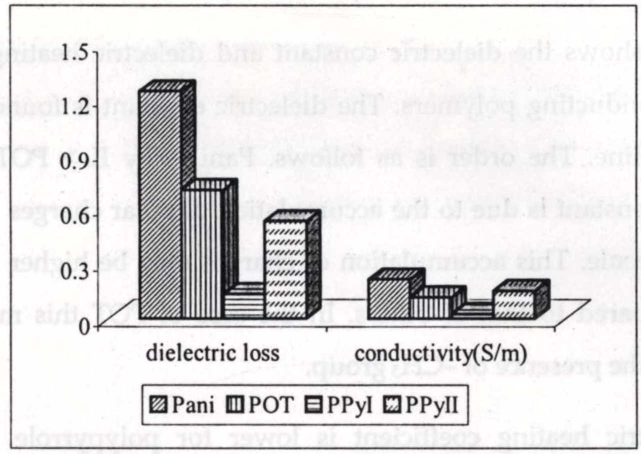


Fig.6.1: Dielectric loss and conductivity of conducting polymers at 2.97 GHz

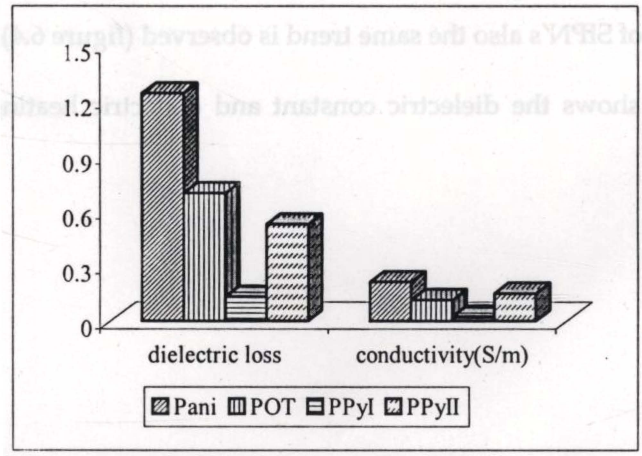


Fig.6.2: Dielectric loss and conductivity of conducting SIPN's at 2.97 GHz.

2. Dielectric constant and dielectric heating coefficient (J)

Figure 6.3 shows the dielectric constant and dielectric heating coefficient of different conducting polymers. The dielectric constant is found to be highest for polyaniline. The order is as follows. Pani >PPy II > POT > PPy I. The dielectric constant is due to the accumulation of polar charges at the interface of the molecule. This accumulation of charges may be higher for polyaniline when compared to that of others. In the case of POT this may be reduced because of the presence of $-CH_3$ group.

The dielectric heating coefficient is lower for polypyrrole. The dielectric heating coefficient is defined as $J = 1/\varepsilon_r \tan \delta$. The loss tangent $\tan \delta$ is directly related to the dielectric loss and inversely related to the dielectric constant and therefore the heating coefficient is highly depend on these factors. The lower the J value the better will be the material for dielectric heating applications. The dielectric heating coefficient follows the order PPy I< Pani< POT< PPy II. In the case of SIPN's also the same trend is observed (figure 6.4)..

Figure 6.4 shows the dielectric constant and dielectric heating coefficient of SIPN's.

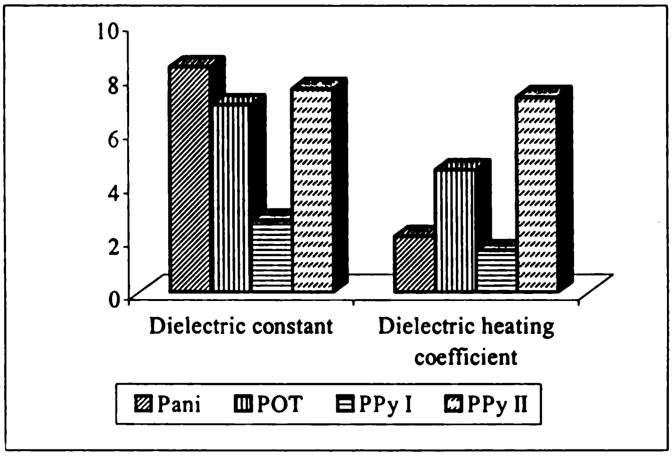


Fig 6.3: Dielectric constant and dielectric heating coefficient of conducting polymers at 2.97GHz

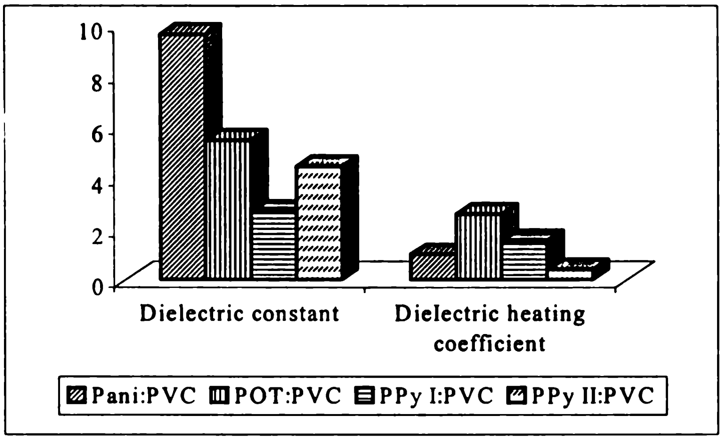


Fig.6.4: Dielectric constant and dielectric heating coefficient of SIPN's at 2.97GHz.

3. Absorption coefficient ($\alpha_{(f)}$) and Skin depth or penetration depth ($\delta_{(f)}$).

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 material the absorption coefficient is very high and the skin depth (the factor indicating the penetration of wave in to material) is minimum. Polyaniline shows a high dielectric loss and hence high absorption coefficient as shown in the figure 6.5.

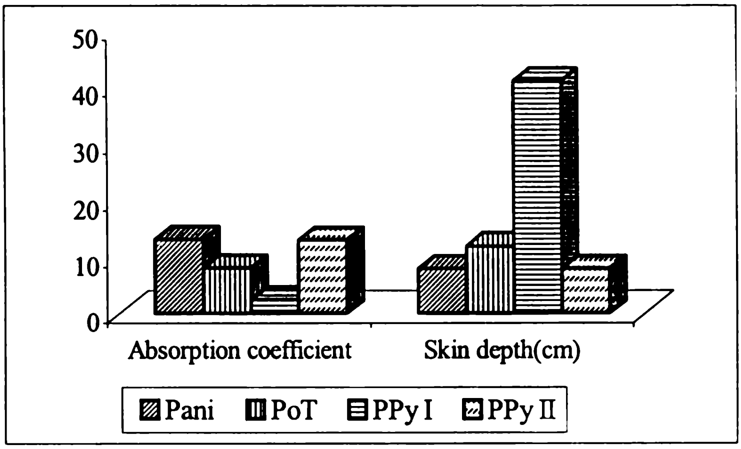


Fig. 6.5: Absorption coefficient and skin depth at 2.97GHz.

The skin depth of polyaniline is lower when compared to other polymers. Polypyrrole prepared using ammonium persulfate also shows a comparable result. In the case of SIPN's the skin depth is minimum for Pani: PVC SIPN and the PPy: PVC SIPN's prepared in different route show comparable result.

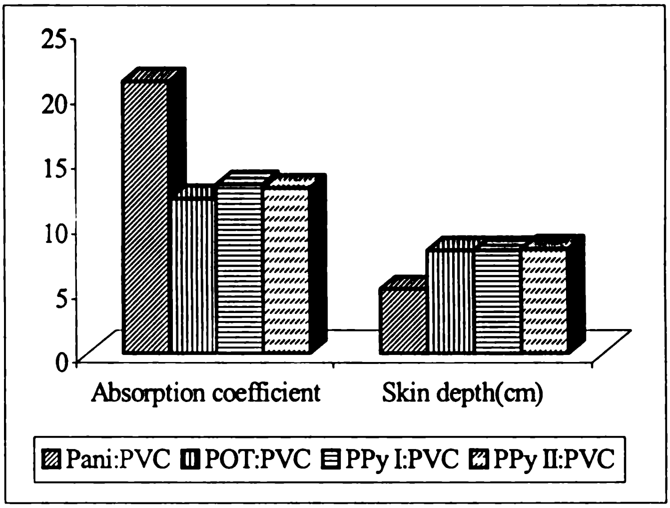


Fig 6.6: Absorption coefficient and skin depth of SIPN's at 2.97GHz.

The results show that the dielectric properties like dielectric loss, conductivity, absorption coefficient and dielectric constant are higher and the dielectric heating coefficient and skin depth are lower for polyaniline and its SIPN. The values of absorption coefficient and skin depth of polypyrrole are comparable with that of polyaniline. Polyaniline shows better values for all other parameters and is also cost-effective.

4. Comparison of polyaniline and the SIPN in pellet form.

The dielectric properties like dielectric loss, dielectric constant, conductivity and absorption coefficient are found to be higher for the SIPN and the heating coefficient and skin depth are lower for the SIPN as shown in table 6.1. The dielectric loss is higher for SIPN because of the interfacial polarisation in the presence of PVC. This is also due to the high dopant concentration because of the presence of PVC (the -Cl of PVC may help to generate more polar centers).

This leads to a higher dielectric loss. The dielectric constant is higher for SIPN due to the accumulation of polar centers at the inter phase between different phases of the molecule.

Table 6.1 : Dielectric properties of polyaniline alone and its SIPN at 2.97GHz

	$\varepsilon''r$	σ(S/m)	ε'	J	$\alpha_{(f)}$ (/m)	$\delta_{(f)}$ (m)
Pani alone	1.24	.21	8.4	2.1	13.2	.08
Pani:PVC SIPN	2.13	0.35	9.6	0.995	21	.05

(b) Film samples

The table 6.1, 6.2, 6.3 compare the dielectric properties of SIPN's of polyaniline, poly o-toluidine, polypyrrole in the S band, C band and X band respectively.

Table 6.2:dielectric properties at S band (at 2.97 GHz)

	$\varepsilon''r$	σ (S/m)	$\varepsilon'r$	J	$\alpha_{(f)}$ (m^{-1})	$\delta_{(f)}$ (m)
Pani:PVC	76	12.549	65.88	0.0122	235	.004
PoT:PVC	4.62	0.76	11.7	0.34	40.5	0.02
PPy:PVC	2.72	0.6	8	0.63	27.6	0.004

Table 6.3: Dielectric properties at C band (at 7.56 GHz)

	ε"r	σ (S/m)	ε'	J	$\alpha_{(f)}$ (/m)	$\delta_{(f)}$ (m)
Pani:PVC	0.33	0.14	2.17	7.73	18	0.06
POT:PVC	2.14	0.91	5.3	0.73	41	0.02
PPy:PVC	0.225	0.1	2.9	16.09	10.5	0.10

Table 6.4: dielectric properties at X band (at 11.98 GHz)

	ε"r	σ (S/m)	ε'	J	$\alpha_{(f)}$ (/m)	$\delta_{(f)}$ (m)
Pani:PVC	.55	.36	2	3.5	47.3	0.02
PoT:PVC	023	0.15	2.8	15.5	25.6	0.317
PPy:PVC	0.41	0.27	3.43	6.96	27.62	0.04

Table 6.2 shows that the dielectric loss, conductivity, dielectric constant and absorption coefficient are high and skin depth, dielectric heating coefficient are low for polyaniline based SIPN. The skin depth of polyaniline SIPN is very low which shows that it is a very good microwave absorber. The reasons for the better properties obtained for polyaniline SIPN are similar as explained in the previous section. Comparison across bands reveals that in C and X bands the dielectric properties are lower when compared to that of S band. At higher frequencies the dipoles will not get enough time to align with the field in an a.c. field and therefore the dielectric properties of all SIPN's in the higher bands are poor. At C band POT:PVC SIPN shows better properties when

compared to Pani:PVC and PPy:PVC SIPN's as shown in table 6.3. At X band Pani: PVC SIPN shows higher dielectric properties compared to the other SIPN's (table 6.4). This indicates the selective absorption nature of Pani: PVC SIPN. Most of ISM (industrial, scientific and medical) applications are in the S band and the polyaniline semi inter penetrating networks is the best choice for this purpose.

(a) Comparison of Pani:PVC SIPN's in pellet and film forms

The important dielectric properties of pellet and film form of Pani: PVC SIPN's are shown in table 6.5. It is clear from the table that the dielectric loss and conductivity is higher for film samples compared to pellet samples. The higher the dilution of matrix the greater the conductivity and therefore the film samples show higher dielectric loss and conductivity than pellet samples. The film sample shows minimum heating coefficient since the dielectric loss of film form is high when compared to pellet samples. The figure also shows the absorption coefficient is high and skin depth is low for film sample and will be a very useful material for microwave applications. From all these results we can say that the Pani: PVC SIPN in film form is the best compared to all other SIPN's studied. Also the processing difficulty of conducting polymers can be overcome in preparing Pani: PVC SIPN in film as it can be easily solution casted or be applied as coating for different applications.

Table 6.5: Dielectric properties of pellet and film samples of Pani:PVC(1:1.5)

	$\varepsilon''r$	σ (S/m)	$\alpha_{(f)}$(/m)	$\delta_{(f)}$(m)	$\varepsilon'r$	J
Pellet	1.24	.21	13.2	.08	8.4	2.1
Film	**76**	**12.55**	**236**	**.004**	**65.8**	**.0122**

PART II

6.2 APPLICATION STUDY

Based on different dielectric properties of Pani: PVC SIPN certain applications are recommended.

1. Antistatic coatings

The dielectric loss of Pani: PVC in film form is very high i.e., 76 and the conductivity are 12.549 S/m. The high dielectric loss indicates that the material is best for anti static coating applications because the static current can be easily discharged as heat. The film form enables the coating easily because it is a solvent soluble SIPN.

2. EMI shielding

Table 6.6 shows the absorption coefficient and skin depth of Pani:PVC SIPN in film form at different frequencies of S band. It is clear from the table that the absorption coefficient is very high and the skin depth is very low at all frequencies. Therefore this material is efficient for EMI shielding applications.

Table 6.6: Absorption coefficient and skin depth of Pani: PVC SIPN(film form).

Frequency(GHz)	Absorption Coefficient(m^{-1})	Skin Depth(m)
2.44	223	.004
2.68	226.5	.004
2.97	235	.004

3. Frequency selective surfaces

The SIPN's especially Pani: PVC in film form shows a high absorption value at S band, a low value at C band and a medium value at X band as shown in table 6.7. This selective nature can be utilized to develop a frequency selective surface.

Table 6.7: Absorption coefficient of Pani:PVC SIPN in film form at S, C, X bands.

	Absorption Coefficient(m^{-1})
S band(at 2.97 GHz)	236
C band(at 7.56 GHz)	18
X band(at 11.98 GHz)	47.3

4. Anti static chappels.

An antistatic chappel is prepared by using pani: NR (2:1) SIPN. The SIPN is prepared by the in situ polymerization of aniline in the presence of natural rubber latex as explained in chapter 3. The SIPN is coagulated and doped with 1 M HCl, washed, dried and it was used for preparing the chapel. The chapel compound was prepared by using the formulation given in table 6.8. Four mixes are prepared i.e., A1 to A4 with varying Phr of 2:1 Pani: NR SIPN.

Table 6.8: Formulation

MATERIAL	A1	A2	A3	A4
NR	70	70	70	70
HSR	30	30	30	30
ZnO	5	5	5	5
Stearic acid	6	6	6	6
Micro crumb	40	40	40	40
Clay	60	60	60	60
Silica	10	10	10	10
Paraffin oil	4	4	4	4
SP	1	1	1	1
Vulcafor F	1.2	1.2	1.2	1.2
S	2.3	2.3	2.3	2.3
DNPT	6	6	6	6
CBS	1	1	1	1
TMTD	.2	.2	.2	.2
Pani:NR SIPN	0	2	4	6

The table 6.9 shows the conductivity and dielectric loss of antistatic chapels prepared using the above formulation. It is clear that the conductivity and dielectric loss of the compound is slightly increased, which indicates that the compound can dissipate current as heat energy.

Table 6.9: Dielectric loss and conductivity of chappal

Phr of Pani :NR(2:1)	Dielectric Loss	Conductivity(S/m)
0 Phr	0.034	$4 * 10^{-5}$
2 Phr	0.163	$2.03 * 10^{-4}$
4 Phr	0.235	$2.9* 10^{-4}$
6 Phr	0.257	$3.2* 10^{-4}$

6.3 CONCLUSIONS

- The dielectric loss and conductivity values follow the order Pani>POT>PPy[$(NH_4)_2S_2O_8$] > PPy[$FeCl_3$]
- The conductivity of SIPN's follows the order Pani:PVC> PPy[$(NH_4)_2S_2O_8$] >POT> PPy[$FeCl_3$]
- The dielectric constant of polyaniline is higher and dielectric heating coefficient is lower than POT and PPy.
- The dielectric constant of SIPN follows the order Pani:PVC> PPy[$(NH_4)_2S_2O_8$] >POT> PPy[$FeCl_3$]
- The dielectric heating coefficient follows the order Pani: PVC< PPy [$FeCl_3$]< PPy [$(NH_4)_2S_2O_8$] <POT.
- The absorption coefficient of Pani: PVC is higher and the skin depth is lower than other SIPN's.
- The film form of Pani: PVC SIPN give better dielectric properties when compared to other SIPN's.
- The absorption coefficient of Pani: PVC SIPN in film form is very high and its skin depth is very low.
- Among all the conducting polymers and SIPN's the Pani: PVC SIPN in film form is the best.

PART III

6.4 FUTURE OUT LOOK

1. *Development of polymer battery*

The preliminary studies on Pani: PVC SIPN shows that the 1:1.5 composition of film form of SIPN can store current. Also it can conduct electricity. This property can be utilized to develop lightweight, very compact and very cheap polymer batteries.

2. *Development of beam steering antennas in radar*

The dielectric constant of all SIPN's are found to vary with variation in the frequency. Also the dielectric loss varies with frequency. It is observed that the main beam of a SIPN embedded dielectric rod antenna gets shifted by applying voltage across it. This property can be utilized for the development of materials for beam steering in radar.

3. *Studies of the effect of temperature and pressure on the dielectric properties of all SIPN's in the microwave field.*

The preliminary studies show that the dielectric properties in the microwave field are very much influenced by temperature and pressure. This property can be utilized to develop pressure and temperature sensors.

Chapter 7

SUMMARY AND CONCLUSIONS

Microwave absorbing materials open up a new vista to various technological applications like EMI shielding, frequency selective surfaces, beam steering antennas, anti static coatings, satellite communication links and dielectric heating applications. In this thesis,we have studied the dielectric properties of selected conducting polymers in the microwave region. Another objective of the work has been to develop cost effective conducting composites having high microwave absorbing capacity with good processability. The development of conducting semi interpenetrating networks based on (polyvinyl chloride) and natural rubber gives stiff competition to conventional conducting polymers used in electrical and microwave applications. The attractive features of conducting composites 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. Another aim of the present study is to link these dielectric properties with various microwave and electrical applications.

A description of the evolution and properties of organic conducting materials and the new area of applications opening up are based on the material is given. A brief introduction of the π conjugated polymers, its charge carriers and the various applications of these systems are also given. The essential properties of a conducting polymer, its mechanisms and important technological applications of have been discussed in detail. A brief history about the synthesis of various conducting polymers, its advantages and disadvantages and the ways to improve the processability of conducting polymers are listed. The recent trends in the field of conducting polymers and their applications in the microwave field are highlighted. The significance of conducting polymers in the microwave field and the major research works done in this area are discussed briefly. The objectives of the present study are also listed.

The wide area of applications of conducting polymers lead to an exploitation of microwave properties like dielectric constant, dielectric loss, conductivity, dielectric heating coefficient, absorption coefficient and penetration depth, of technologically important conducting polymers like polyaniline, poly o-toluidine and polypyrrole. The dielectric properties of these polymers in the microwave frequencies are dependent on many chemical and physical parameters such as synthesis conditions, drying condition, nature of dopant and the concentration of dopant. It is observed in the present study that the room temperature preparation gives better dielectric properties compared to the conventional low temperature synthesis. The effect of drying conditions of polyaniline, poly o-toluidine and polypyrrole on their dielectric properties has been investigated. The HCl dopant is found to contribute most efficiently to the microwave field compared to many other dopants like camphor sulfonic acid, toluene sulfonic acid, H_2SO_4, $HClO_4$, HNO_3. In the case of polypyrrole, chemical oxidative polymerisation using ammonium per sulphate as the initiator gives better microwave properties compared to the usual ferric chloride initiated synthesis. A copolymer of poly (o-toluidine co aniline) is prepared which shows better dielectric properties compared to poly o-toluidine in the microwave frequencies.

Inorder to improve the processability of conducting polymers investigated semi interpenetrating networks (SIPN) of these polymers and other polymers are prepared. The dielectric properties of such SIPN's have also been investigated. SIPN's like Pani:PVC, POT:PVC and PPy:PVC are found to very promising combination in view of their improved processability and dielectric properties. The dielectric properties like dielectric loss, conductivity and absorption coefficient are very high compared to polyaniline, polyo-toluidine and polypyrrole. The properties like dielectric heating coefficient and penetration depth are very low for the SIPN's, which favour the microwave applications. In addition to the powder and pellet form of SIPN's, cyclohexanone soluble conducting SIPN's are prepared. The soluble form gives better dielectric properties in the microwave frequencies compared to powder and pellet forms.

A significant finding of this study is that the presence of a basically nonconductor 'PVC' can improve the dielectric properties of a conducting polymer in addition to improving the processability. It is also very peculiar that the PVC loading increases the dielectric loss, conductivity and absorption coefficient of the SIPN up to a particular proportion. The dielectric heating coefficient and penetration depth is the lowest for this particular proportion. In the case of polyaniline - PVC SIPN the 1:1.5 composition in all forms i.e., powder, pellet and film gives the best dielectric properties. In the case of poly o-toluidine (POT:PVC) 1:3 proportion for pellet and film forms and in the case of polypyrrole matrix (PPy:PVC) 1:2 proportion in pellet form, 1:3 proportion in film form, yields best results.

The dielectric properties of the matrices studied are supported by the IR spectroscopy, Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Scanning Electron Microscopy(SEM).

A detailed comparison of the dielectric properties of all conducting matrices used in the present work is done. Among all the conducting polymers, polyaniline shows the highest conductivity and absorption coefficient. The dielectric heating coefficient and penetration depth is lowest for polyaniline. Similarly the dielectric properties of Pani: PVC SIPN is better when compared to other SIPN's. The soluble form of Pani:PVC SIPN is the best for dielectric applications since it gives high conductivity (12.57 S/m), high dielectric loss (76), high absorption coefficient [>250 (m^{-1})], very low dielectric heating coefficient (.002) and low penetration depth (.004 m).

Flexible conductive polyaniline / Natural Rubber (Pani/NR) semi interpenetrating networks is prepared using the in-situ polymerization technique. This SIPN is also found to be a very significant combination as conducting natural rubber. These interesting dielectric properties of SIPN's of polyaniline reveals the applications of conducting composites in various fields like antistatic coatings, frequency selective surfaces, antistatic chappals, EMI shielding etc. Future applications of this conducting SIPN are also listed in this thesis.

LIST OF PUBLICATIONS

1. **"Complex permittivity and conductivity of poly aniline at microwave frequencies"** S.Bijukumar, Honey John, Rani Joseph, M.Hajian, L.P.Ligthart, K.T.Mathew, *Journal of European ceramic society, Vol.21, 2672-2680,(2001).*
2. **"Effect of drying condition on the microwave conductivity of poly aniline" Honey John, S.Bijukumar, K.T.Mathew, Rani Joseph,***Journal of Applied polymer science,* Vol.83, 2008-2012(2002)
3. **"Studies on conducting poly aniline-polyvinyl chloride composite"** Honey John, S.Bijukumar, K.T.Mathew, Rani Joseph, *Rubber, plastics, composites, (accepted for publication)*
4. **"Studies on the dielectric properties of poly o-toluidine and poly(o-toluidine-aniline) copolymer"** Honey John, Rinku M.Thomas, K.T.Mathew, Rani Joseph, *Journal of Applied polymer science (accepted for publication)*
5. **"Studies on the dielectric properties of polyaniline / polyvinyl chloride semi interpenetrating netwoks in the microwave field"** Honey John, Rinku M.Thomas, K.T.Mathew, Rani Joseph, Communicated to *Macromolecules.*
6. **"Studies on the dielectric properties of polyaniline/ natural rubber composite in the microwave field"** Honey John, K.T.Mathew, Rani Joseph, Communicated to *Polymer journal.*
7. **"Studies on the dielectric properties of polyo-toluidine and its semi intrpenetrating networks with polyvinyl chloride",** Honey John, K.T.Mathew, Rani Joseph, Communicated to *Synthetic Metals.*

8. **"Effect of synthesis on the dielectric properties of polypyrrole and its composite with polyvinyl chloride"**
   Honey John, K.T.Mathew, Rani Joseph, *International Conference on Materials for Advanced Technologies 2003 (ICMAT 2003),*(Accepted)
9. **"Studies on the dielectric properties of polyaniline-polyvinyl chloride semi inter penetrating net works"**
   Honey John, K.T.Mathew, Rani Joseph, *Proceedings of Kerala state Science congress -2003 (Young Scientist Award 2003)*
10. **"Microwave studies on the dielectric properties of poly(pyrrole-polyvinyl chloride)semi inter penetrating polymer networks"**
    Honey John, K.T.Mathew, Rani Joseph, *Proceedings of international seminar, APT 2002*
11. **"Novel electrically conducting polymers"** Honey John, K.T.Mathew, Rani Joseph, *Proceedings of Kerala state Science congress -2002*
12. **"Studies on the dielectric properties of poly(o-toluidine-polyvinylchloride) semi inter penetrating net works"** Honey John, Joe Jacob, K.T.Mathew, Rani Joseph, *Proceedings of APSYM, 2002.*
13. **"Studies on the dielectric properties of poly (pyrrole-poly vinyl chloride) semi inter penetrating polymer networks"**, Honey John, K.T.Mathew, Rani Joseph, *14 th Annual General Meeting MRSI, Bombay, Feb 11-13, 2003.*

LIST OF ABBREVIATIONS

%	Percentage
$(NH_4)_2S_2O_8$	Ammonium per sulfate
π	Pi
^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
FeCl3	Ferric chloride
fs	Frequency
GHz	Giga hertz
gm	Gram
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
$HClO_4$	Perchloric acid
HNO_3	Nitric acid
Hz	Hertz
I_2	Iodine
IR	Infra red
J	Dielectric heating coefficient
KHz	Kilo hertz

m	Meter
M	Molar
MHz	Mega hertz
min	Minutes
nm	Nanometre
NR	Natural rubber
Pani	Polyaniline
PoT	Poly o-toluidine
PPy	Polypyrrole
PPy I	Polypyrrole prepared using ferric chloride as the initiator
PPy II	Polypyrrole prepared using Ammonium per sulfate as the initiator
PVC	Polyvinyl chloride
S	Seimen
sec	Seconds
SEM	Scanning electron microscopy
SIPN	Semi inter penetrating networks
$\tan \delta$	Loss tangent
TGA	Thermo gravimetric analysis
$\alpha_{(f)}$	Absorption coeffient
$\delta_{(f)}$	Penetration depth
ε'_r	Dielectric constant
ε''_r	Dielectric loss
π	pi
ρ	Resistivity
σ	Conductivity