STUDIES ON CONDUCTING POLYMERS AND CONDUCTIVE ELASTOMER COMPOSITES

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COCHIN UNIVERSITY OF
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PRINCY K. G.

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KOCHI- 682 022

JUNE 2002

Certificate

*This is to certify that this thesis entitled "**Studies on Conducting Polymers and Conductive Elastomer Composites**" is a report of the original work carried out by Smt. Princy K. G. under our supervision and guidance in the Department of Polymer Science and Rubber Technology. No part of the work reported in this thesis has been presented for any other degree from any other institution.*

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DECLARATION

*I hereby declare that the thesis entitled "**Studies on Conducting Polymers and Conductive Elastomer Composites**" is the original work carried out by me under the supervision of Dr. Rani Joseph, Professor, Department of Polymer Science and Rubber Technology, and Dr. C. Sudha Kartha, Reader, Department of Physics, Kochi 682 022, and no part of this thesis has been presented for any other degree from any other institution.*

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to

my

family

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Princy K. G.

PREFACE

Conducting polymers, because of their unusual properties, have attracted great interest in recent years. Despite the short history, they have found a place in various applications. This thesis is about the development of conductive silicone rubber and nitrile rubber; and the synthesis, characterization and properties of novel conducting polymer –poly (p-phenylenediazomethine) and their blends with polyethylene, PVC and silica.

This thesis is divided into seven chapters as follows:

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 into three parts; Part-I reports the effect of different types of carbon blacks [e.g., acetylene black, lamp black, and ISAF (N-234) black], copper powder, and graphite on the electrical conductivity and mechanical properties of silicone rubber. Part –II reports the effect of different types of carbon blacks [e.g., N-220, N-347, and N-339 carbon blacks] on the electrical conductivity and mechanical properties of silicone rubber. The effect of temperature on the conductivity of silicone rubber vulcanizates is also studied. Part-III reports the effect of blending silicone rubber with high-density polyethylene on the conductivity and mechanical properties of the vulcanizates.

Chapter 4 is divided into two parts; Part I deals with the effect of concentration of acetylene black on the electrical conductivity and mechanical properties of nitrile rubber vulcanizates. Part II deals with the effect of blending of NBR with other polymers on the electrical conductivity and mechanical properties of the vulcanizates at the same dosage of acetylene black. Preparation of nitrile rubber blends with NR, EPDM and PVC and the measurement of electrical conductivity and mechanical properties are reported. Part III deals with the variation in conductivity and mechanical properties of the vulcanizates with different composition of NBR/NR blends at the same dosage of acetylene black. Part –IV deals with the effect of temperature on the electrical conductivity of these vulcanizates.

Chapter 5 includes the synthesis and characterization of a new conducting polymer based on glyoxal and p-phenylene diamine. The synthesis of poly(p-phenylenediazomethine) was carried out in different solvents, like, methanol, toluene, m-cresol and DMF. D.C. conductivity, dielectric properties and thermal diffusivity of the polymer prepared in different solvents were determined. Effect of dopants on the d.c. conductivity and dielectric properties was also investigated.

Chapter 6 includes in-situ polymerization of glyoxal and p-phenylenediamine in different solvents containing different amounts of PE, PVC, and silica. The d.c. conductivity and microwave conductivity of each sample was measured. The effect of dopants like $HClO_4$, HCl and I_2 on conductivity was also studied.

Summary and conclusions of the present investigation is described in the last chapter, **Chapter 7**.

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

Contents

Chapter 1

INTRODUCTION

The possibility of improving the conductivity of polymers, which are conventionally insulators, to metallic levels has attracted not only chemists, but also physicists and even material scientists. Many researchers have tried to combine the processability and other attractive properties of polymers with the electronic properties of metals or semiconductors. Conducting polymers are different from electrically conductive polymers as they are conductive only if the individual conductive particles are in contact and form a coherent phase[1].

A major breakthrough in the search for conducting polymers occurred in 1977[2-4] with the discovery that polyacetylene could be readily oxidized by electron acceptors such as iodine or arsenic pentafluoride or reduced by donors such as lithium. The resulting material had a conductivity that was orders of magnitude greater than the original, untreated sample. The redox reaction can be carried out in the vapour phase, in solution, or electrochemically.

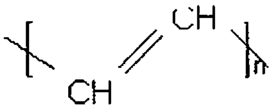
A significant development occurred in 1979 with the discovery [5] that poly (p-phenylene) could also be doped with AsF_5 to high conductivity. It demonstrated that polyacetylene is not unique and this led to the development of a number of new poly aromatic-based conducting systems, including poly (p-phenylene sulphide) [6,7], polypyrrole[8], polythiophene[9], and polyaniline[10].

Another important development was the discovery of conducting polymer solutions. Films with high conductivity and mechanical integrity can be cast from these solutions. Composites and blends are also being investigated as means for processing and shaping conducting polymers for a wide spectrum of applications[11,12].

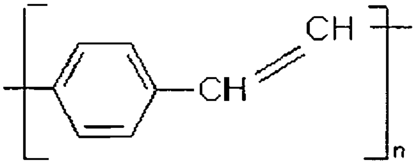
1.1 Synthesis of conducting polymers

Since the conductivity of conducting polymers are known to depend on the method of synthesis, a large number of preparatory methods have been developed to improve the conductivity. Addition, condensation, electrochemical, ring opening, and plasma polymerisation are the most notable and widely used techniques in this regard. Other methods include Diels-Alder elimination, Wittig reaction, Ziegler-Natta catalysis, Friedel Crafts reaction and nucleophilic displacement reaction. In designing polymer synthesis, the incorporation of extended pi-electron conjugation is of foremost importance.

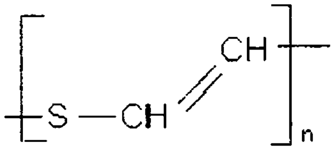
Polyacetylene films are prepared by exposure of acetylene gas to smooth surfaces wetted with solutions of the Ziegler-Natta polymerisation catalyst[3]. It exists predominantly as the cis isomer with a high degree of crystallinity. Isomerization to the more stable trans form can be induced by heat or dopants[3, 13-16] . Polyacetylene can also be synthesized by the retro Diels Alder reaction [17,18]. Copolymers of acetylene units alternate with an electron rich unit include polyvinylenephenylene[19], poly(vinylenesulfide)[20], and poly(vinylenephenylenepyrrole)[21].



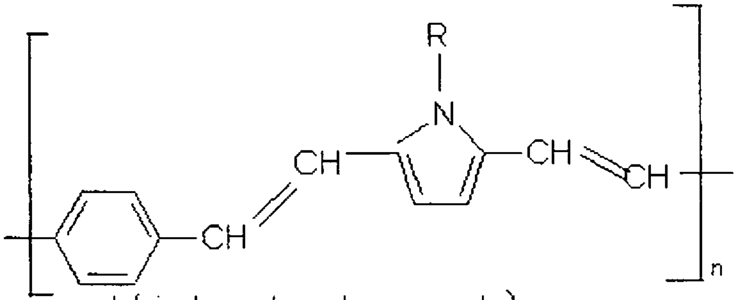
polyacetylene



poly(vinylenephenylene)

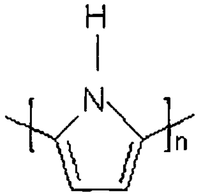


poly(vinylene sulfide)

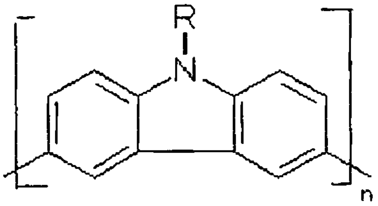


poly(vinylenephenylene pyrrole)

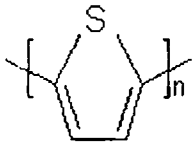
Polymers of heterocycles such as pyrrole and thiophene can be viewed as derivatives of polyacetylene in which adjacent olefinic moieties have been bridged with nitrogen or sulphur. Pyrrole and its alkylated derivatives are usually polymerised electrochemically from a solution of the appropriate monomer[22]. Typically, application of a potential of 0.5 V between two electrodes in an acetonitrile solution containing $AgClO_4$ electrolyte and pyrrole monomer proceeds with the accumulation of an oxidized polypyrrole film on the anode. This film, as prepared, is conductive, since it incorporates inorganic counter ions (ClO_4^- ion) from the solution as it is oxidatively synthesized. In a similar manner other conducting polymers have been prepared electrochemically, including polythiophene[23,24], polycarbazole, polyazulene, and polyisothianaphthene[25]. Electrochemical polymerisation offers the advantages of homogeneous incorporation of dopant counter ions into the polymer film as it is grown and control over the polymerisation parameters of current density and voltage. The method is limited, however, by the fact that the yield of polymer is restricted to the area of working electrode in the electrochemical apparatus.



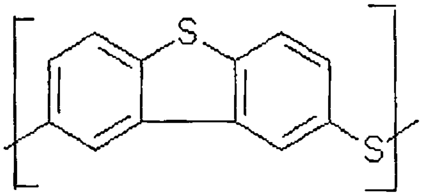
polypyrrole



polycarbazole



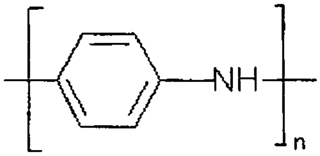
polythiophene



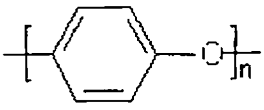
poly(dibenzothiophene sulfide)

Polymers containing phenyl group constitute a large class of conducting polymers, which are thermally, and oxidatively more stable than other polymers. Phenyl rings are there in the polymer backbone as repeat units in aniline (polyaniline), phenol (Poly(p-phenylene oxide)), thiophenol (poly(p-phenylene sulphide)), or simply as phenyl (poly(p-Phenylene)).

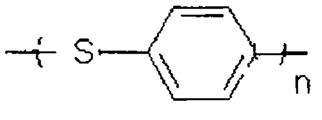
Poly(p-phenylene) is obtained when benzene is coupled by aluminium chloride/cupric chloride at 35 ^{0} C in benzene solvent [26] . Poly(p-phenylene oxide), which can be rendered conducting by doping has been prepared by an Ullman condensation of sodium p-bromophenolate [27,28] . Poly (p-phenylene sulphide) can be industrially prepared by the high temperature coupling of sodium sulphide and p-dihalobenzene[29]. Polyaniline is an electro active organic polymer that displays good environmental stability. The acid doped polymer is the precipitated product from an aqueous solution containing ammonium per sulphate, hydrochloric acid and aniline [30,31]. Variations of the synthesis of polyaniline have included electrochemical techniques [10,32] and different solvent/acid media.



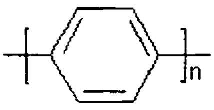
polyaniline



poly(p-phenylene oxide)



poly(p-phenylene sulphide



poly(p-phenylene)

1.2 Doping

The conductivity 'σ', of any conducting material is proportional to the product of the free-carrier concentration, n, and the carrier mobility, μ,

$$\sigma = e n \mu$$

where 'e' is the unit electronic charge. Since conjugated polymers have relatively large band gaps, the concentration of free carriers is very low at normal temperatures. Therefore, even though conjugated polymers have high carrier mobility, the low carrier concentration results in low conductivity.

Doping is a process in which a virgin polymer is treated with a strong oxidizing or reducing agent that either abstracts electrons from the polymer or donates electrons to it through the formation of a charge carrier into the polymer for the enhancement of it's conductivity.

$$\text{Polymer} + \text{acceptor dopant} \xrightarrow{\text{(oxidation)}} (\text{polymer}^{+}\,\text{dopant}^{-})$$

$$\text{Polymer} + \text{donor dopant} \xrightarrow{\text{(reduction)}} (\text{polymer}^{-}\,\text{dopant}^{+})$$

The doping of conjugated polymers increases the carrier concentration. Doping in polymers is a redox process involving charge transfer with subsequent creation of charged species. With polymers, electronic excitations are accompanied by a disorder or relaxation of the lattice around the excitation, and thus structural and electronic excitation will result in structural defects along the polymer chain. Removal of an electron leaves an unpaired spin near the valence band (p- doping) and addition of an electron fills the corresponding state near the conduction band (n- doping)[33].

Oxidative dopants are usually electron-attracting substances. The common p-type dopants are Br_2, I_2 , AsF_5, H_2SO_4, $HClO_4$, BCl_3 , PF_5 , SbF_6 , CH_3F, NO_2F, NO_2, $NO^+SbCl_6^-$, SO_3, $FeCl_3$, etc. n-type dopants are electron donating substances like sodium naphthalide, Na/K alloy, molten potassium, LiI etc.. There are a number of ways by which doping can be carried out. Essentially, these different methods can be broadly summarized as being solution doping, vapour phase doping and electrochemical doping.

In conducting polymers the doping process can be reversed, i.e, the conducting polymer can be converted to insulator by neutralization back to the uncharged state. This return to neutrality is called compensation. Exposure of oxidatively doped polymer to electron donors, or, conversely, of reductively doped polymers to electron acceptors effects compensation. This property is made use of in the construction of rechargeable batteries.

1.3 Temperature characteristics of conductors

The temperature characteristics are of importance when considering possible applications for conductors. Generally speaking, the conductivity of a metal falls as the temperature is raised because of the scattering of the carriers and this is recognized by an increase in resistance. In this case, the temperature coefficient of the resistance is positive (PTC). If the temperature of a semiconductor such as silicon is raised the conductivity increases because of the rise in the number of carriers. Such materials are said to have a negative temperature coefficient (NTC). The situation with a typical macromolecular conductor such as polyacetylene differs according to the doping concentration.

Even though many conducting polymers show metallic level of conductivity, the temperature dependence of conductivity is not like metal. In most of the cases, the dependence is like that of a semiconductor. The semiconductor like behaviour of conductivity can be explained on the basis of the existence of potential barriers between highly conducting regions. These barriers are due to conjugational defects or other inhomogeneities in the polymer chain. The charge carriers will have to hop or tunnel through the potential barriers. Since tunnelling by itself is a temperature independent process, the temperature dependence of conductivity must arise from other processes influencing the charge transfer between highly conducting regions. The models of Sheng[34], take into account the charging energy of conducting regions of the random thermal motion of charge carriers on both sides of the tunnel junction[35], and the derived transport characteristics have been the most successful ones in describing the conductivity of highly doped conjugated polymers.

When the size of highly conducting regions or islands are sufficiently small (less than 20nm), the energy required to move an electron from an electrically neutral island become significant. If the voltage between two adjacent islands is small compared to kT/e, charge carriers can be generated only by thermal activation, making conductivity temperature dependent and limited by only the charging energy. The charge carriers will then percolate along the path with least resistance. The conductivity varies with temperature as [34],

$$\sigma\ (T) = \sigma_0 \exp\{(-T_0/T)^{1/2}\}$$

where σ_0 and T_0 are material constants.

If the size of the highly conducting regions is larger than about 20nm, charging energy becomes negligible. Sheng's second model for inhomogeneous conductors is based on fluctuation-induced tunneling of charge carriers between highly conducting islands. This model applies to larger conducting regions, typically of the order of a micrometer. The theory assumes that the random thermal motion of the charge carriers within the conducting islands induces a randomly alternating voltage across the gap between neighbouring islands. The temperature dependence of the conductivity arises from thermal fluctuation-induced tunnelling of charge carriers between highly conducting island [35] and is expressed as follows:

$$\sigma\ (T) = \sigma_1 \exp\{-T_1/(T_2+T)\}$$

where T_1 and T_2 are material constants depending on the width and height of the tunnelling barrier[36].

Effects such as doping resulting in inhomogeneously distributed dopants, fibrillar morphology, interchain transport, transport through grain boundaries etc. can be well explained by the above mentioned models.

The values of the conductivity at zero temperature are a distinguishable difference between tunnelling and hopping conduction. Since tunnelling between localized electronic states is phonon assisted , the hopping conductivity vanishes as the temperature falls to zero. Since tunnelling process is temperature independent, and depends only on the height and shape of the potential barrier separating the carriers, conductivity does not extrapolate to zero. As the temperature is decreased, fewer states fall within the allowed energy range and the average hopping distance increases. As a result, the hopping probability and thus, conductivity decrease.

1.4 Electrical conductivity and carrier transport

A great deal of work had been done for the characterization and understanding of electrical transport in conducting polymers. The factor limiting the conductivity is the carrier mobility, along with the carrier concentration. The doping process produces a generous supply of potential carriers, but to contribute to conductivity they must be mobile. There are at least three elements contributing to the carrier mobility: single chain or intramolecular transport, interchain transport, and interparticle contact. These three elements comprise a complicated resistive network (illustrated in the Fig. 1. 1), which determines the effective mobility of the carriers. Thus, the mobility and therefore the conductivity are determined on both a microscopic (intra- and interchain) and a macroscopic (interparticle) level [37].

In conjugated polymers, ionisation results in substantial distortion of the lattice around the ionised states, similar to all organic materials. So, as a charge carrier moves through the polymer, due to this distortion of the lattices, mobility is reduced. Since disorder plays such a dominant role in conducting polymer systems, the mechanism of carrier transport is more akin to that in amorphous semiconductors (hopping transport) [38].

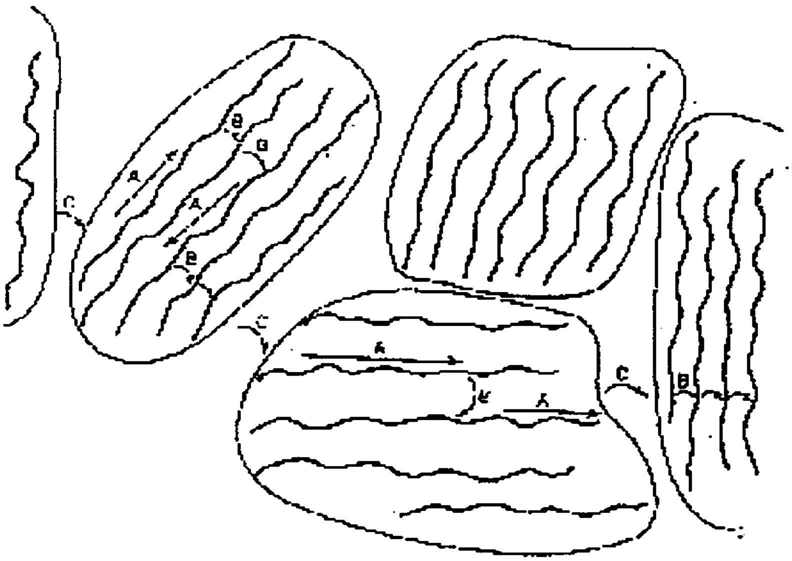


Fig.1.1 Conductivity network of a conducting polymer with A indicating intrachain transport of charge, B indicating interchain transport, C indicating interparticle transport, and arrows showing path of a charge carrier migrating through the material

1.5 Charged defects in conjugated polymers : Theory of conduction

The theoretical work on conducting polymers has been mainly concerned with radical and ionic sites, referred to as neutral and charged defects, respectively. The movement of the defect can be described mathematically as a solitary wave, or "soliton" in the language of field theory [39-42]. The radical defect is referred to as a neutral soliton; the anion and cation defects are charged solitons. Charged solitons (anions or cations) can explain the spinless transport, since they carry charge but no spin.

The initial species formed on the ionisation of a conjugated polymer is a radical ion, which possess both spin and charge[43, 44]. In the language of solid-state physics, the radical ion is referred to as a polaron. A polaron is either a positively charged hole site (radical cation) or a negatively charged electron site (radical anion), plus a lattice relaxation (distortion) around the charge. Theoretical models[43] demonstrate that two radical ions (polarons)on the same chain react exothermically to produce a dication or dianion (bipolaron) ,which are responsible for spin less conductivity in these polymers.

1.6 Microwave conductivity

All dielectric materials are characterized by their dielectric parameters such as dielectric constant, conductivity and polarization[45-47]. In conjugated polymers, ionisation results in substantial distortion of the lattice around the ionised states, similar to all organic materials. So, as a charge carrier moves through the polymer, due to this distortion of the lattices, mobility is reduced. Since disorder plays such a dominant role in conducting polymer systems, the mechanism of carrier transport is more akin to that in amorphous semiconductors (hopping transport) [38].

Microwave technology owes its origin to the design and development of Radar. In the earlier stages of development, phased array technique is used for the beam steering in Radar. It is a very complicated design and it needs mechanical work for the beam steering. Poly o-toluidine can easily undergo a dipolar polarization when the microwave frequency is applied[48]. This property can be utilized for developing systems for electronic beam forming in Radar. The materials with low D.C. conductivity, but high microwave conductivity (poly o-toluidine) can be used to develop microwave communication link[48]. It is also very useful in satellite communication, i.e, to prohibit stray signals and to allow the passage of microwave signals.

The determination of the complex permittivity and conductivity is based on the theory of perturbation. When a dielectric material is introduced in a cavity resonator at the position of maximum electric field, the contribution of magnetic field for the perturbation is minimum.

In microwave studies the conductivity can be calculated using the equation,

Conductivity, $\sigma = 2\pi f_s \varepsilon_0 \varepsilon_r''$

where 'f' is the resonant frequency, ε_0 is the permittivity of vacuum and ε_r'' is the imaginary part of the complex permittivity , which is given by the equation,

$\varepsilon_r'' = (V_c / 4V_s)(Q_t - Q_s / Q_t Q_s)$

where,' V_c ' is the volume of cavity, V_s is the volume of sample, Q_s is the quality factor of the cavity loaded with the sample and Q_t is the quality factor of the cavity with the empty sample holder. Quality factor 'Q' is given by

$Q = f / \Delta f$

where 'f' is the resonant frequency and ' Δf ' is the corresponding 3dB bandwidth. The real part of the complex permittivity 'ε_r' is usually known as dielectric constant of the material. It can be calculated from the equation,

$\varepsilon_r' = 1 + (f_t - f_s)/ 2f_s (V_c / V_s)$

where ' f_t ' is the resonant frequency of the unloaded cavity and ' f_s 'is the resonant frequency of the cavity loaded with the sample. The imaginary part, ε_r'' of the complex permittivity is associated with dielectric loss of the material.

1.7 Poly (azomethine)s

Poly (azomethine)s, sometimes called poly(schiff bases), are a group of polymers which are catching more attention due to the following reasons. Fully aromatic poly (azomethine)s are highly thermo-stable in analogy to aromatic polyethers. Further more, fully aromatic poly (azomethine)s may possess a conjugated main chain and, after suitable doping, may show an attractive level of electric conductivity.

Most polycondensations of aromatic dialdehydes and diamines were conducted in solutions[49]. Three kinds of solvents were used: benzene and toluene[50-52] to allow azeotropic removal of water, polar aprotic solvents, such as DMF, DMA, NMP or DMSO[53-57] or, protic solvents such as acetic acid and m-cresol[58]. Regardless of solvent most aromatic poly (azomethine)s are insoluble in common organic solvents and precipitate from the reaction medium, in particular if they are built up by para-substituted monomer units. Precipitation entails an almost complete stop of the chain growth process, and thus, strongly limits the resulting molecular weights. Azeotropic distillation of water with benzene or toluene accelerates the condensation and enhances the yields, but it does not significantly increase the degree of polymerisation, which is limited by the solubility of the polymers in the reaction medium. In this regard polar aprotic solvents, or the aforementioned protic solvents are advantageous, because poly (azomethine)s are better soluble in these polar reaction media. When the reaction is carried out in m-cresol at 200^{0}C, the polymers remained in solution over the whole course of the condensation and the molecular weight of the polymer is comparatively high.

Only a few poly (azomethine)s derived from aliphatic dialdehydes and aromatic diamines were described in literature, and most of them were prepared by solution condensation of diamines and glyoxal [59-61]. High yields and satisfactory elemental analyses were reported, but no information on viscosity and molecular weights.

In the present study, the monomers, glyoxal and p-phenylene diamine was selected for the synthesis of a new conducting polymer. P-phenylene diamine introduces an aromatic ring in the polymer that helps to increase the thermal stability of the polymer. Solvents selected for carrying out the condensation reactions are methanol, DMF, m-cresol and toluene, which include all types of solvents mentioned above. This helps to compare the properties of the polymer formed under different conditions.

1.8 Conducting polymer blends

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[62-64]. Most of the conducting polymers are insoluble in common organic solvents and so the casting of it into film or other forms that are useful for different applications is very difficult. Similarly, conducting polymers like polyacetylene are unstable in air and their conductivity changes with time due to their interaction with air, oxygen, etc. The major drawbacks of conducting polymers like environmental instability and difficult processibility can be overcome by preparing their composites with other polymers. 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[65]. Interpenitrating network conducting composites result though in situ polymerization of monomers of conducting polymers inside the matrices of the conventional linear polymers.

Conducting polymer blends with unusually low percolation threshold has been reported for polyaniline and styrene –butyl acrylate copolymer blends[66]. Polyaniline – Epoxy Novolac Resin composite has been reported to be useful for antistatic applications[67]. Interpenetrating networks of polypyrrole filaments in swellable insulating plastic matrices have been produced in electrochemical cells[68,69].

1.9 Electrically Conductive Elastomers

Elastomers and plastics are insulators to which conductivity is imparted by the addition of finely divided or colloidal filler of high intrinsic conductivity, such as carbon black. Conductive rubber compounds were first put to use for the prevention of corona discharge in cables. Large quantities of graphite or other coarse carbon blacks or powdered metals were employed to produce conductivity in rubbers. Addition of acetylene black and other conductive blacks yielded conductive rubber with improved mechanical properties. Rubbers filled with furnace black showed antistatic properties. Non-insulating antistatic rubbers are now used in many situations where explosive (or inflammable) vapours , liquids, or powders are being handled. Effect of temperature on conductivity follows Arrhenius type of equation and estimation of activation energy for electrical conduction is possible. Conductive rubbers are used in various disciplines. E.g. sensors, electrochromic displays, EMI shielding, electrostatic discharge dissipation (ESDD), conductive pressure sensitive rubbers, fuel cells, circuit boards etc[70].

The basic and generally accepted concepts of conductivity are based on the fact that carbon black forms aggregates or network structures in the compositions[71-72]. The degree of conductivity depends on the nature of these chain structures. In recent years papers relating to the effect of various factors influencing the conductivity of polymer compositions containing carbon black have been published- like type of carbon black[71, 72], concentration of carbon black[72], type of polymer[73,74], temperature[72,75] and degree of dispersion of carbon black in the polymer matrix[76,77]. The effect of mixing time on electrical and mechanical properties on SBR vulcanizates has been reported[78].

Bulgin[79] has critically analyzed the importance of cure conditions with reference to the electrical properties. The effect of processing parameters on resistivity of NR vulcanizates is also reported[80]. Jana [81] reports electrical conduction in short carbon fibre filled polychloroprene composites. Abo-Hashem etal.[82] reports the effect of concentration and temperature dependence of butyl rubber mixed with SRF carbon black.

1.10 Conductive fillers

For many years, finely divided carbon black has been a valuable addition to electrically conductive polymers, including rubber compounds and the resulting composite materials exhibit a wide spectrum of conductivity depending on the loading of the carbon black. It is used to enhance their conductivity and cost effectiveness. Many grades like channel black, thermal black, furnace black, acetylene black etc. are available from the combustion of hydrocarbon feed stocks. The high structure and surface area of conducting carbon blacks facilitate the contact probability of aggregated carbon black by decreasing the particle –to-particle distance. Sometimes carbon black can be hybridised with carbon fibre in compounding so as to reach the optimum electrical conductivity, enhanced mechanical properties, and improved processability.

Acetylene blacks have been attractive to compounders desiring high electrical conductivity. X-ray spectrographic analysis shows acetylene black to have, in part, a graphite structure with a lace-like acicular or fibrous aggregate of carbon particles. About 70% of the particles occur in the 25 to 60 nanometer size range. 'Vulcan" XC-72 carbon black also appears to fall in this range of good electrically conductive carbon black. "ketjen" carbon black is also well recommended. Furnace blacks produced by thermal decomposition of oil fed stocks, and channel blacks produced by natural gas flames on water-cooled channel iron have prominent roles in materials used by the plastics and the rubber industry[83-84].

Other conductive additives are:- polyacrylontrile (PAN) carbon fiber, metal-coated carbon fiber and in particular nickel-coated graphite fiber, stainless steel fibers, aluminium fibers, metallized glass fibers, aluminium flakes, metal powders, metal-coated glass beads, metal-coated mica and graphite powder.

1.11Electrical conduction in carbon black loaded rubber vulcanizates

The particles of carbon black are not discrete but are fused 'clusters' of individual particles[84,85]. These aggregates are the working unit in vulcanized rubber. At low loadings of carbon black, the conductivity of the composite is very low. It is shown that starting at a certain level, an increase in the amount of carbon black in a composition leads to a marked increase in conductivity and this then tends asymptotically to a finite value. The entire region of conductivity increase is called the percolation region. In this region, conductivity is limited by barriers to passage of the charge carries (electrons) from one carbon black aggregate to another, which is close but not touching. The electron must surmount a potential barrier to get out of the carbon black aggregate and cross the gap.

In 1957 Polley and Boonstra[86] proposed that electrons "jump" across this gap. Five years later, van Beek and van Pul[87] proposed that electron passage in these systems is due to tunneling which is a special case of internal field emission. In the case of carbon black filled composites, Sheng, Sichel and Gittleman[35], have shown that a special type of tunneling, activated by thermal fluctuations of the electric potential, is the dominant mechanism.

According to Medalia[88], the tunneling current is an exponential function of the gap width; thus tunneling takes place between very closely neighbouring carbon black aggregates, with virtually no conduction between aggregates, which are separated by somewhat larger gaps. As the loading density is increased, the aggregates are more tightly packed and pressed against each other. This results in reduction of internal contact resistance, and hence conductivity increases. Once a high enough loading is reached, so that contact resistance between aggregates is no longer significant, further increase in loading would not be expected to cause any significant increase in conductivity. Thus at high loading, "through going chains" are formed.

In summary, it appears that for composites at normal loadings and normal temperatures, the dominant mechanism of conduction is either tunneling through the gap, assisted by thermal fluctuations, or thermal activation of electrons over the potential barrier of the gap. For conductive blacks at high frequencies and high loadings, conduction is not limited by the electron transport across the gap but by the intrinsic conductivity of the carbon black (i.e., within the carbon black aggregates)

The "structure" or bulkiness of the carbon black aggregates also affect the conductivity similar to that of loading, since aggregate of higher structure occupy, in effect , a higher volume of the composite[89]. Janzen's theory [90] predicts that high-structure blacks should have a low percolation threshold, and at a given loading, a high- structure black would have a higher conductivity than a low-structure black.

The conductivity depends considerably on the state of dispersion of the black in the percolation region. Experimentally, the conductivity of a carbon black-rubber composite increases rapidly during the very stages of mixing, as carbon black is incorporated and pathways are established between the islands of rubber-filled pellet fragments; and the conductivity then decreases gradually during the later stages of mixing, as the agglomerates are broken down and the gap between individual aggregates is increased[91-92].

Particle size of the carbon black also influences the conductivity of carbon black loaded rubbers. The conductivity decreases with increasing particle size of the carbon black It has been argued [86] on purely geometric grounds, that smaller particle size should lead to smaller gap width and leads to more conducting paths per unit volume. It has also been suggested that[88] the smaller particles arrange themselves more easily into chains than do the coarser types.

Effect of temperature on the conductivity of various elastomer-carbon black composites is reported. Abo-Hashem etal[82] reports that the variation of conductivity with temperature below the percolation threshold was characterized by thermally activated behavior above a certain temperature. The temperature dependence of conductivity above the percolation threshold was attributed to both breakdown and re-formation of carbon clusters with temperature. At ordinary and elevated temperatures, rubber compounds with normal loadings of carbon black show a decrease in conductivity with increase in temperature[93-95]. This is due to increase in gap width due to the thermal expansion of the rubber. Compounds with very low loadings show the reverse behavior. At relatively high temperature, conductivity is increasingly activated with increasing temperature. Here rubbers behave like semiconductors and follow the Arrhenius equation;

$$\sigma = C \exp(-E_a/kT)$$

in which C is a pre-exponential factor and E_a represents an activation energy. In this region, the distance between carbon black aggregates becomes large enough to give rise to extrinsic conduction, and the conductivity originates mainly in the charge carriers of the rubber matrix.

1.12 Elastomer blends

All rubbers have shortcomings in one or more properties. Therefore, by blending two rubbers, it should be possible to obtain the right compromise in properties[96]. Blending can reduce the difficulties experienced in processing some rubbers. There are economic reasons also for blending the rubbers.

Polymer blends are mixtures of structurally different homopolymers, co-polymers, terpolymers and the like. They can be homogeneous (miscible) or heterogeneous (multi-phase). Many polymer pairs are known to be miscible or partially miscible, and many have become commercially important. The criteria for polymer/polymer miscibility are embodied by the equation for the free energy of mixing

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

where ΔG_m is the change in Gibbs Free energy, ΔH_m the change in enthalpy, ΔS_m the change in entropy upon mixing and T is the absolute temperature. The necessary condition for miscibility is that $\Delta G_m < 0$. Hence, two polymers can be expected to be miscible only when there is a very close match in cohesive energy density or in specific interactions, which produces a favourable enthalpy of mixing. Most blends of elastomers are immiscible because mixing is endothermic and the entropic contribution is small because of high molecular weight. True miscibility is not required for good rubber properties even though, adhesion between the polymer phases is necessary and the respective interfacial energies are important in this respect[97]. The following definitions are assigned for the various classes of polymer blends:

i. Polymer blends (PB): the all-inclusive term for any mixture of homopolymers and copolymers.

ii. Miscible polymer blends: a class of PB referring to those blends which exhibit single phase behavior

iii. Immiscible polymer blends: a subclass of PB referring to those blends that exhibit two or more phases at all compositions and temperature.

iv. Partially miscible polymer blends: a subclass of PB including those blends that exhibit miscibility only at certain concentrations and temperature.

v. Compatible polymer blends: a utilitarian term, indicating commercially useful materials, a mixture of polymers without strong repulsive forces that is homogeneous to the eye.

vi. Interpenetrating polymer network (IPN): a subclass of PB reserved for mixtures of two polymers where both components form continuous phases and at least one is synthesized or cross linked in the presence of the other.

1.12.1 Silicone rubber/HDPE blends

Silicone rubber can be blended with other elastomers and plastics like polyethylenes[110]. This makes it possible to obtain a sufficiently high electrical conductivity with reduced filler content owing to the accumulation of carbon black in the phase of one of the polymers. By mixing silicone rubber with polyethylenes, vulcanizates with high electrical conductivity along with good mechanical properties can be prepared. The property of high temperature stability and chemical resistance are maintained in the conducting vulcanizates.

1.12.2 NBR/NR blends

The blending together of NR and NBR is carried out with the intention of producing a vulcanizate with the best properties of the two components, for example, nitrile rubber's high oil resistance and NR's good strength properties. NR and NBR widely differ in polarity and hence maldistribution of cross-links can arise through preferential solubility of the curatives and vulcanisation intermediates in one of the phases. The difference in polarity of the rubbers causes high interfacial tension. NR and NBR have quite different solubility parameters and this limited degree of mixing at the interface of a blend.

The amount of conductive fillers required to impart conductivity to NBR/NR blend is very low due to the selective localization of the conductive filler at the interface of these two components or in any one of the phase.

1.12.3 NBR/EPDM blends

NBR has excellent oil resistance but is subject to degradation at high temperature and addition of antidegradents is not effective. Further, NBR is a polar rubber and is fast curing than EPDM. EPDM has excellent resistance to ozone and oxygen and hence excellent weatherability even without antioxidants and antiozonants. NBR/EPDM blend was prepared with the intention of producing a vulcanizate with the best properties of the two components.

The amount of conductive fillers required to impart conductivity to NBR/EPDM blend is very low due to the selective localization of the conductive filler at the interface of these two components or in any one of the phase.

1.12.4 NBR/PVC blends

Miscibility of polymer blends was first observed with NBR/PVC systems. NBR having an acrylonitrile content in the range of 25 to 40 wt.% is completely miscible with PVC[98,99]. Small amount of NBR in PVC can improve the impact strength of rigid PVC compositions. The properties of NBR/PVC blends are sensitive to blending conditions and variations in the individual polymers used.

NBR acts as a solid plasticizer for PVC and at the same time PVC improves the ozone, thermal ageing and chemical resistance of NBR. NBR of certain composition exhibits compatibility with PVC that is unusual among polymers[100]. NBR can produce compatible and semi compatible blends with PVC according to the acrylonitrile content of the rubber.

1.13 Conductive elastomer blends

The amount of electrically conductive fillers required to impart high electrical conductivity to an insulating polymer can be dramatically decreased by the selective localization of the filler in one of the phase or at the interphase of a continuous two-phase polymer blend [101-106]. Not only the final cost of the material is decreased, but the problems associated with an excess of filler on the processing and mechanical properties of the final composites are alleviated. The localization of carbon black in an immiscible polymer blend is basically controlled by the mutual polymer-polymer and polymer –filler interaction [107-108]. When carbon black is localized at the interface of continuous polyethylene/polystyrene [103] and polystyrene/polyisoprene[104] blends, the carbon black percolation threshold may be as small as 0.2 %. Sircar has observed that carbon black originally dispersed in a rubber migrates to the interface with another immiscible rubber as a result of more favourable interactions with this second polymeric component[106]. An improved electrical conductivity is observed when several conditions are fulfilled (i) the two rubbers must be immiscible, (ii) there must be a large difference in the carbon black-rubber interactions and (iii) the rubber less interacting with carbon black should be less viscous.

El- Mansy and Hassan[109] reports the electrical conductivity of NR/SBR rubber composites filled with HAF black. The variation in conductivity with the amount of carbon black and temperature is the same as that in the case of a single elastomer.

1.14 Scope and objectives of the present work

At present conductive rubbers are being imported at a high cost. So the development of conductive rubbers in India is of prime importance. The primary aim of this work have been the development of conductive silicone rubber, which is used for making conductive pads in telephone sets and calculators. The work envisages the comparison of electrical conductivity and mechanical properties of silicone rubber vulcanizates loaded with different amounts of acetylene black, lamp black and ISAF black. The effect of temperature on these vulcanizates also proposed to be studied with the intention of generating a conductive rubber, which can be used for long-term and /or high temperature applications. Nitrile rubber is also proposed to be loaded with varying amounts of acetylene black and the mechanical properties and electrical conductivity of the vulcanizates are proposed to be studied. Conductive nitrile rubber vulcanizates may be advantageously used where mechanical strength and oil resistance is needed along with electrical conductivity.

Since polymer blends are likely to show higher conductivity than pure elastomers when loaded with the same amount of acetylene black, the effect of conductive fillers on the conductivity and mechanical properties of silicone rubber / nitrile rubber is also proposed to be investigated. Silicone rubber is proposed to be blended with high-density polyethylene and nitrile rubber with polyvinyl chloride, ethylene propylene diene rubber and natural rubber.

The specific objectives of the work can be summarised as follows: -

1. To develop conducting silicone rubber vulcanizates with high temperature stability and good mechanical properties.
2. To develop nitrile rubber vulcanizates with good electrical conductivity and mechanical properties.
3. To prepare a new conducting polymer based on p-phenylene diamine and glyoxal – poly(p-phenylenediaminedizomethine) - , which has high thermal stability.
4. To prepare blends of the newly prepared polymer with polyethylene, polyvinyl chloride, and silica to improve the processability and to decreases cost of the conducting polymer.
5. To study the d.c. conductivity and microwave conductivity of the conducting polymer and their blends.

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Chapter 2

EXPERIMENTAL TECHNIQUES

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

2.1 Materials Used

2.1.1 Polymers

1 Silicone rubber

Silicone rubber used in the present investigation was general-purpose silicone rubber supplied by GE Silicones, having the following specifications:

Hardness	40 (Shore A)
Grade	FSE 7140
Density, g/cm^3	1.41
Appearance	Neutral

2 High density polyethylene (HDPE)

High-density polyethylene used was Indothene HD, supplied by Indian Petrochemical Corporation Ltd, Vadodara, which had the following properties:

Density, gm/cm^3	0.957
Melt flow index (gm/10 min)	5.2

3 Nitrile rubber (NBR)

Nitrile rubber (NBR), used in the present study was supplied by Apar India, Mumbai that had the following specifications:

Grade	Aparene N-553 NS
Acrylonitrile content	33%
Mooney viscosity [ML (1+4)] at 100^0C	48

4 Natural rubber (NR)

Natural rubber used was solid block rubber ISNR-5 grade obtained from Rubber Research Institute of India, Kottayam, having the Mooney viscosity [ML (1+4)] at $100^0C = 85.3$. 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 mater, 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

5 Ethylene -propylene-diene rubber (EPDM)

Ethylene –propylene-diene rubber used has the following specifications:

Grade	SR EP 33
Ethylene content	33 mole%
Diene content	1 mole%
Mooney viscosity [ML (1+4)] at 100^{0}C	52.

6 Low density polyethylene (LDPE)

Low-density polyethylene used was Indothene 24 FS 040 grade obtained from Indian Petrochemical Corporation Ltd, Vadodara, which had the following properties

Density, gm/cm^3	0.922
Melting range ,^{0}C	105-110
Melt flow index at 190^{0}C (gm/10 min)	6.0

7 Polyvinylchloride (PVC)

Polyvinyl chloride used was Emulsion grade having the K value 70.5, supplied by Indian Petrochemical Corporation Ltd, Vadodara.

2.1.2 Additives

1 Acetylene black (AB)

Acetylene black used in the study was supplied by Travancore Electrochemicals, Kerala, having the following specifications:

Average EM particle diameter	41 nm
Dibutylphthalate (DBP) absorption	310 mL 100g^{-1} .

2 High structure ISAF black (N-234)

High structure ISAF black used was supplied by Cabot India Ltd. (Mumbai, India), having the following specifications:

Average particle diameter	23 nm
DBP absorption	125 mL 100 g^{-1}

3 Lamp black (LB)

Lamp black used was supplied by Cabot India Ltd.(Mumbai) , with an average particle diameter, 100 nm.

4 High Structure HAF black (N-339)

Improved High Structure HAF (N-339) black used was supplied by Cabot India Ltd. (Mumbai, India), having a D B P absorption of 120 mL 100 g^{-1} and average particle diameter of 26 nm.

5 High Structure HAF black (N-347)

High Structure HAF (N-347) black used was supplied by Cabot India Ltd.·(Mumbai, India), having a DBP absorption of 124 mL 100 g^{-1} and average particle diameter of 27 nm.

6 Intermediate Super Abrasion Furnace black (ISAF, N- 220)

Intermediate Super Abrasion Furnace (ISAF, N- 220) black) used was supplied by Cabot India Ltd. (Mumbai, India), with a DBP absorption of 114 mL 100 g^{-1} and average particle diameter of 21 nm.

7 Graphite powder

Graphite powder used in the study was supplied by Asian Minerals (Chennai), having the following specifications:

Density, g/cm^3	2.25

Mohs' hardness	1.0

8 Copper powder

Electrolytic purpose grade copper powder supplied by E. Merck (India) Ltd.,Mumbai, was used in the present study, having the following Specifications;

Density, g/cm^3	8.94
Melting Point, ^{0}C	1083
Mohs' hardness	3.0

9 40% active dicumyl peroxide (DCP)

Dicumyl peroxide used was a crystal with a purity of 99% and density, 1.02 (gm cm^{-3}). The recommended processing temperature of the material is 160-200^{0}C.

10 Zinc Oxide (ZnO)

Zinc Oxide was supplied by M/s Meta Zinc Ltd; mumbai, having the following specifications:

Specific gravity	5.5
Zinc Oxide content	99.5 %
Acidity	0.4 % max
Heat loss (2 hours at 100^{0}C)	0.5% max

11 Stearic acid

Stearic acid used in the study was supplied by Godrej Soaps (Pvt) Ltd; Mumbai having the following specifications.

Melting point	50-69^{0}C
Acid number	185 – 210

Iodine value	9.5 max

12 Dibenzthiazyl disulphide (MBTS)

Dibenzthiazyldisulphide used in the study was supplied by Bayer Chemicals, Mumbai and had the following specifications:

Specific gravity	1.34
Melting point	165^{0}C

13 Tetramethyl thiruam disulphide (TMTD)

Tetramethylthiuramdisulphide (TMTD), was supplied by ICI India Ltd., Mumbai, having the specifications:

Specific gravity	1.42
Melting point	140^{0}C

14 Sulphur (S)

Sulphur (soluble), was supplied by Standard Chemical Company Pvt. Ltd., Chennai having the following specifications:

Specific gravity	2.05
Acidity	0.01% max
Ash	0.01% max
Solubility in CS_2	98% max

15 Dioctylphthalate (DOP)

Dioctylphthalate used was commercial grade, supplied by Rubo-Synth Impex Pvt. Ltd., having the following specifications:

Specific gravity	0.986
Viscosity, cps	60

16 Magnesium oxide (MgO)

Magnesium oxide used was commercial grade calcined light magnesia with a specific gravity of 3.6, supplied by Central Drug House Pvt. Ltd., Mumbai.

2.1.3 Materials used in the synthesis

1 Para-phenylene diamine (PPD)

Para-phenylene diamine used for the synthesis was LR grade, supplied by Central Drug House (P) Ltd., Mumbai, having the following specifications:

Melting point	141^{0}C
Boiling point	267^{0}C

2 Glyoxal

Glyoxal used for the synthesis was of two types:

(a) Glyoxal 40 % solution, supplied by Kemphasol, Mumbai, having the following specifications:

Density, g/cm^{3}	1.29
Boiling point	51^{0}C and

(b) Glyoxal hydrate (trimer) for synthesis, supplied by Merck-Schuchardt, Hohenbrunn, which is colourless crystalline powder.

3 N,N-Dimethyl formamide (DMF)

N,N-Dimethyl formamide used had an assay (GC) of 99.5%, boiling point of 153 ^{0}C, density of 0.9445 g/cm ^{3} and was supplied by E. Merck (India) Ltd., Mumbai.

4 m-Cresol

m-Cresol used was 98 % pure , LR grade, supplied by Central Drug House (P) Ltd., Mumbai, having boiling point of 202°C and density of 1.034 g/cm^3.

5 Toluene

Toluene used in the present study was sulphur free, LR grade, supplied by s.d. fiNE-CHEM Ltd., Mumbai, having boiling point of 110°C and density of 0.866 g/cm^3.

6 Methanol

Methanol used in the present study was AR grade, supplied by s.d.fiNE-CHEM Ltd., Mumbai having boiling point of 65°C and density of 0.7866 g/cm^3.

6 Tetrahydrofuran (THF)

Tetrahydrofuran used was supplied by E. Merck (India) Ltd., Mumbai, having boiling point of 66°C and density of 0.8892 g/cm^3.

8 Acetone

Acetone used in the present study was LR grade, supplied by s.d.fiNE-CHEM Ltd., Mumbai.

9 Silica

Silica used was Ultracil VN-3, having a surface area of 170 m^{2}g^{-1} and particle size range 11-19 nm, supplied by United Silica Industrial Ltd., Taiwan.

10 Hydrochloric acid (HCl)

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

11 Perchloric acid ($HClO_4$)

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

12 Iodine (I_2)

Iodine used was LR grade, supplied by Qualigens fine chemicals, Mumbai.

13 Carbon tetra chloride (CCl_4)

Carbon tetra chloride used was supplied by E. Merck (India) Ltd., Mumbai.

14 Sodiumhydroxide (NaOH)

Sodiumhydroxide used in the present study was LR grade, supplied by s.d.fiNE-CHEM Ltd., Mumbai.

2.2 Experimental methods

2.2.1 Brabender Mixing

Brabender Plasticorder (a type of torque rheometer made by M/s Brabender OHG Duisburg, Germany, Model PL 3S) has been widely used for polymer blending, processability studies of polymers, modelling processes such as extrusion and evaluation of the rheological properties of the polymer melts [1-5]. The torque rheometer is essentially a device for measuring the torque generated due to the resistance of a material being mixed or flowing under preselected conditions of shear and temperature. The heart of the torque rheometer is a jacketed mixing chamber whose volume is approximately 40 cc for the model used. Two horizontal rotors with protrusions do mixing or shearing of the material in the mixing chamber. The resistance generated by the material is made available with the help of a dynamometer. The dynamometer is attached to a precise mechanical measuring system, which indicates and records the torque. A DC thyrister controlled drive is used for speed control of the rotors (0 to 150 rpm range). Circulating hot silicone oil controls the temperature of the mixing chamber. The temperature can be varied up to 300^0C. Thermocouple with a temperature recorder is used for control and measurement of temperature. Different types of rotors can be employed depending upon the nature of the polymers.

The rotors can be easily mounted and dismounted by simple fastening and coupling system. Once test conditions (rotor, type, rpm and temperature) are set, sufficient time should be given for the temperature to attain the set value and become steady, subsequently the material can be charged into the mixing chamber.

2.2.2 Mill Mixing and Homogenization using Mixing Mill

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

After completion of the mixing, the compound was homogenized by passing six times endwise through a tight nip and finally the batch was sheeted out as very thin sheet (2 mm thickness).

2.2.3 Cure characteristics using Goettfert Elastograph.

The cure characteristics of the compounds were 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.

The following data can be taken from the torque-time curve.

1. Minimum torque: torque obtained by the mix after homogenizing at the test temperature before the onset of cure.
2. Maximum torque: this is the torque recorded after the curing of the mix is completed.
3. Scorch time (t_{10}): this is the time for attaining 10% of the maximum torque.
4. Optimum cure time (t_{90}): This is the time taken for attaining 90% of the maximum torque.
5. Cure rate: Cure rate was determined from the following equation

$$\text{Cure rate (Nm/min)} = (T_{max} - T_{min})/(t_{90} - t_{10})$$

where T_{max} and T_{min} are the maximum and minimum torque respectively and t_{90} and t_{10} are the times corresponding the optimum cure time and scorch time respectively.

The elastograph microprocessor evaluates the vulcanization and prints out these data after each measurement.

2.2.4 Moulding of test specimens

The test specimens for determining the physical properties were molded in standard mould by compression molding in an electrically heated hydraulic press having 45 x 45 cm platens at a pressure of 200 kg/cm^2 in the mould. The rubber compounds were vulcanized up to their respective optimum cure times at specified temperatures. Upon completion of the required cure cycle, the pressure was released and the sheet was stripped off from the mould and suddenly cooled by plunging into cold water. After a few seconds, the samples were taken from the cold water; and stored in a cold dark place for 24 h and were used for the subsequent tests.

2.3 Physical test methods

For parameters described below, at least three specimens per sample were tested for each property and the mean values reported.

2.3.1 Tensile strength, elongation at break and modulus

These parameters were determined according to ASTM D 412 (1980) test method, using dumb bell shaped test pieces. The samples were punched out from the moulded sheets using C-type die along the mill grain direction of the vulcanized sheets. The thicknesses of the narrow portion of specimens were measured using a dial gauge. The specimens were tested on a Zwick universal testing machine (UTM) model 1445 at 28±2^{0}C and at a crosshead speed of 500 mm per minute. The tensile strength, elongation at break and modulus were recorded on a strip chart recorder. The machine had a sensitivity of 0.5 % of full-scale load.

The ultimate tensile strength (TS) of the sample was measured as the force measured by the load cell at the time of break divided by the original cross sectional area of the sample at the point of minimum cross section.

Ultimate tensile strength = Force (N)/cross sectional Area (mm^2)

The elongation at break (EB %) of the sample was measured in terms of its initial length 'L_0' and final length 'L_1' as,

$EB = (L_1 - L_0) \times 100/L_0$

2.3.2 Tear strength

The samples were cut from the compression-molded sheets parallel to the mill grain direction. The test was carried out on a Zwick Universal Testing Machine (UTM) as per ASTM D 624 91981) using the unnicked, 90^0 angle test pieces. The speed of extension was 500 mm/min and the test temperature 28 ± 2^0C.

2.3.3 Hardness

The hardness of the samples was tested using Zwick 3114 hardness tester (shore A) in accordance with ASTM D 2240 (1981). The tests were performed on mechanically unstressed samples. A load of 12.5 N was applied and the readings were taken after 10 seconds of indentation after firm contact had been established with the specimens.

2.3.4 Density

The prepared polymer samples were compressed into pellets in a pelletizer. The mass of the pellet and thickness of the pellet was determined and the volume of the pellet was calculated using the equation, $V= \pi r^2 t$, where'V' is the volume of the pellet, ' r ' , is the radius of the pellet and 't' is the thickness of the pellet. The density of the sample is then calculated from the equation, Density = Mass / Volume

2.3.5 Measurement of D.C. conductivity

The problems due to external electrical pick-ups and varying humidity in the laboratory can be minimized by holding the samples inside a metal chamber as shown in the figure 2.1. Figure 2.1 shows various parts of the conductivity cell. The chamber was well grounded and could be evacuated to 10^{-2} torr so that it acted as a shield to the electrical pick-ups and ambient humidity. The chamber had a metallic cylindrical body of height 30 cm and diameter of 10 cm. It also had a pumping port, which could be connected to a rotary pump. The top of the cell was closed vacuum tight using a circular metal plate, from which a sample holder was connected by welding. This holder was provided with a heater (~40W) in order to vary the temperature of the sample for measurement purposes. The heating rate of the sample can be maintained constant, throughout the experiment by carefully adjusting the voltage. All insulations of the holder were made from Teflon. The heater could go up to ~ 200°C. A chromel-Alumel thermocouple was used to measure the temperature. The electrodes of the holder were copper blocks mounted on Teflon strips. The electrical connections were taken out through BNCs. Shielded cables were used outside the metallic cell, to make connections to d. c. power supply and electrometer.

A steady d.c. power supply (6 V) was used as the voltage source. The current flowing through the sample was measured by a digital multimeter (APLAB model 1087). For low conductivity samples, Keithley 236 Source Measurement Unit was used for the current measurement.

Schematic diagram of experimental setup used for D.C. conductivity measurement in the present work is shown in the figure 2.2. For electrical conductivity measurements the silver electrodes were deposited in the planar rubber sample with a gap in between them. The d.c. voltage was applied across the samples. The voltage was measured using a high impedance digital voltmeter. The electrometer was connected in series with the power supply and the samples. The pressure inside was maintained constant at 10^{-2} torr using a Rotary pump for rubber samples. The measurements were done at atmospheric pressure for the synthesized samples in the pellet form. The temperature was noted by measuring the voltage across the thermocouple. The d.c. bias (6V) was applied as shown in Fig. 2.2 The temperature of the sample was slowly increased at a constant rate using the variable D.C. power supply. Then the current through the sample was monitored using the digital multimeter at different temperatures, from 25^0C to 150^0C.The electrical conductivity, 'σ ' can be calculated using the equation,

σ = Current density 'J'/ Field strength 'E'

J = Current 'I'/ Area' A'

E = Applied voltage 'V'/ Distance between the two electrodes 'd'

i.e., σ = Id / AV

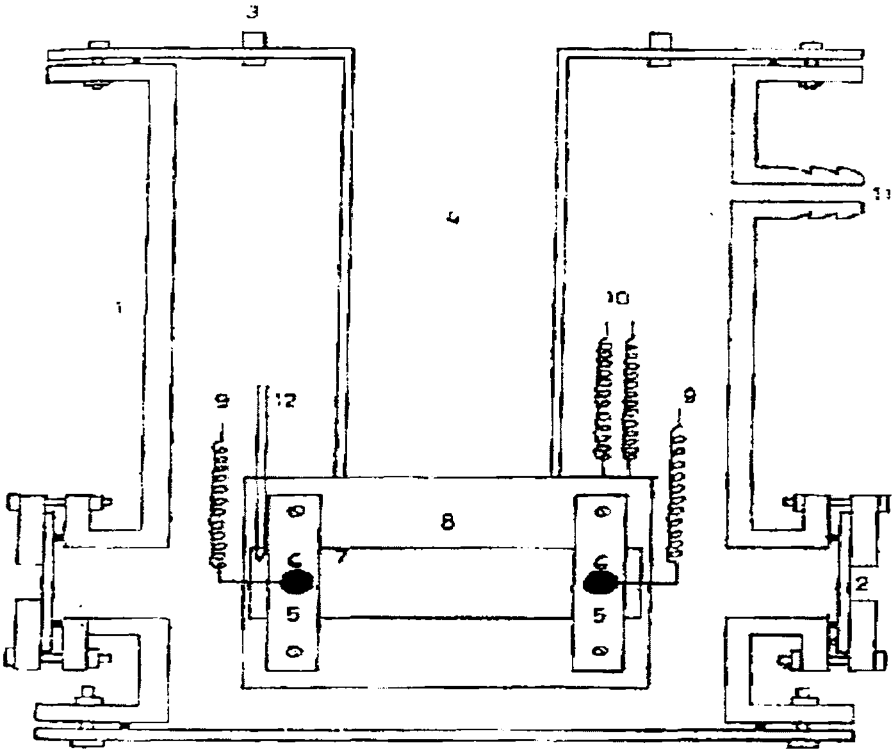
Resistivity is the reciprocal of conductivity.

The temperature dependence of the electrical conductivity is described by an expression of the type

$$\sigma = \sigma_0 \exp(-E / kT)$$

where, σ is the conductivity of the sample at a temperature, T, σ_0 is the constant which is characteristic of the material, E is the energy of activation, and k is the Boltzmann constant.

$$\log \sigma = \log \sigma_0 - (E / kT)$$



1. Metal cylinder
3. B.N.C.
5. Teflon blocks
7. Substrate with film
9. Electrode-BNC inter-connections
11. Pumping ports

2. Glass window
4. LN_2 chamber
6. Electrode
8. Heater/Substrate holder
10. Electrical connections to the heater
12. Thermocouple

Fig. 2.1 Conductivity cell

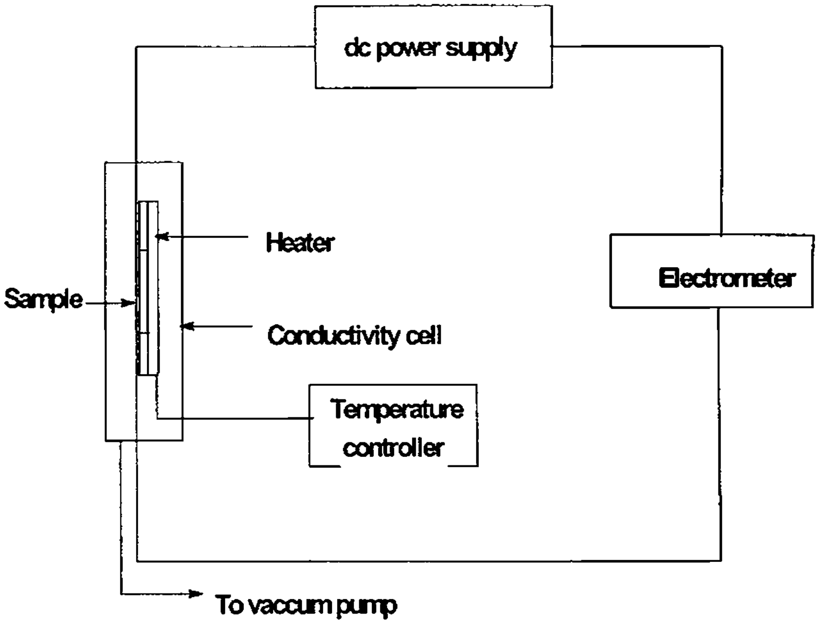


Fig. 2.2 Schematic diagram of experimental set up for d.c. conductivity measurement

2.3.6 Measurement of microwave conductivity

The dielectric properties and conductivity of the samples were measured using cavity perturbation technique[6]. The experimental set up consists of a HP 8510 vector network analyzer, sweep oscillator, S-parameter test set and rectangular cavity resonator. The measurements were done in S-band at 2.17GHz at room temperature (25^0C).

In microwave studies the conductivity can be calculated using the equation,

Conductivity, $\sigma = 2\pi f_s \varepsilon_0 \varepsilon_r''$

where 'f_s' is the resonant frequency, 'ε_0' is the dielectric constant of air and ε_r'' is the imaginary part of the complex permittivity , which is given by the equation,

$$\varepsilon_r'' = (V_c / 4V_s)(Q_t - Q_s / Q_tQ_s)$$

where,' V_c ' is the volume of cavity, 'V_s' is the volume of sample, 'Q_s' is the quality factor of the cavity loaded with the sample and 'Q_t' is the quality factor of the cavity with the empty sample holder.

The real part of the complex permittivity ε_r' is usually known as dielectric constant of the material. It can be calculated from the equation,

$$\varepsilon_r' = 1 + (f_t - f_s) / 2f_s (V_c / V_s)$$

where 'f_t' is the resonant frequency of the unloaded cavity and 'f_s' is the resonant frequency of the cavity loaded with the sample.

The pelletized samples were inserted into the cavity and the perturbations produced at a particular microwave frequency were noted. The resonant frequency and quality factor were recorded and dielectric constant and microwave conductivity were calculated using the above equations.

2.3.7 Thermal diffusivity

Thermal properties of polymeric materials are always important and often critical in both processing stages and product uses. Thermal diffusivity is an important material property, determining the temperature distributions in nonsteady-state heat conduction. It can be defined by the mathematical expression, $\alpha = \kappa / \rho \, c_p$, where '$\kappa$' is the thermal conductivity, 'ρ' is the density and 'c_p' is the specific capacity at constant pressure. In general, thermal conductivity of polymers are quite low and of the order of 0.1 –0.3 x 10^{-6} m^2/Sec.

Thermal diffusivity was determined by photo acoustic technique.

2.3.8 Infrared spectroscopy

Infrared (IR) 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 the characteristic frequencies. The frequency and intensity of absorption are indication of the bond strengths and structural geometry in the molecule. Particles of the polymer samples were flattened by means of cold compression between two diamond windows. IR spectra of the samples were recorded with a Biorad UMA 500infrared microscope, which is coupled to a Biorad FTS 6000 spectrometer. Spectra were recorded with a resolution of 4 cm^{-1} co-adding 100 scans.

2.3.9 Thermo gravimetric analysis (TGA)

TGA measures the change in the mass of a sample as it is heated, cooled, or held isothermally. Therefore, a TGA can detect percentage of moisture and volatiles, percentage of fillers and additives in multicomponent system, compositional difference in blends, degradation temperature and decomposition kinetics study of a sample. The two most important information that can be extracted out of the thertmogram are: (a) the extrapolated onset temperature, which provides indication of the thermal stability of the specimen, and (b) the percentage weight of loss of the components present, which enables quantification of organic polymer and additives. Thermo gravimetric analysis was recorded on Perkin-Elmer TGA-7 instrument at a heating rate of 10^0C/min. from 35^0C to 800^0C in nitrogen atmosphere.

2.3. 10 Molecular weight determination

Molecular weight of the polymer was determined by Gel Permeation Chromatography. GPC (Waters WISP 710 B) equipped with PFG columns, provided by PSS polymer standard services. Measurements were conducted in

Hexa fluoro isopropanol at 25^{0}C at a flow rate of 0.4 ml / min. using a UV detector (Waters 490).

2.3.11 UV- Visible spectroscopy

UV spectra of the palletized polymer samples were taken using HITACHI 330 spectrophotometer.

2.4 References

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Chapter 3

STUDIES ON CONDUCTIVE SILICONE RUBBER VULCANIZATES

3.1 Introduction

The chain structure of silicone rubbers does not involve a long chain of carbon atoms but a sequence of silicon and oxygen atoms. This siloxane structure results in a very flexible chain with extremely weak interchain forces. Hence the silicone rubbers are noted for high heat resistance, low glass transition temperature, high permeability to gases and high compressibility of silicones. Further, the inorganic backbone is responsible for the fungus resistance of silicones and their lack of appeal to rodents[1].

Silicone rubber retains its properties at high temperature. It doesn't contain any carbon - carbon double bonds in the backbone and hence it has high resistance to ozone, oxygen and ultraviolet light. The rubber has good resistance to dilute acids and bases and salts normally found in surface water.

Silicone rubber is odourless, tasteless, and non-toxic. When properly fabricated, it does not stain, corrode, or in any way deteriorate materials with which it comes in contact. So it finds application in gas masks, food and medical-grade tubing, and even in surgical implants in the human body.

A typical silicone rubber formulation contains a silicone polymer, reinforcing and (or) extending fillers, process aids or softeners to plasticize and retard crepe ageing, special additives for heat ageing and flame retardant additives, colour pigments, and one or more peroxide as curing agent.

Silicone rubber may be compounded in conventional equipment, such as Doughmixers, Banburys and two-roll mills.

Electrical conductivity is important in many rubber and plastic goods for antistatic applications, wire and cable sheathing, shielding against electromagnetic interference, etc. Elastomers and plastics are insulators to which conductivity is imparted by the addition of finely divided fillers of high intrinsic conductivity, such as carbon black.[2,3] The structures of carbon blacks and the influence of the structure on the properties of filled rubbers are well established.[2,4,5].

Conductive silicone rubber has received considerable attention, probably because of its stable current time characteristics, controlled thermal coefficient of resistivity, high thermal limits, and capability of being fabricated by conventional techniques. Numerous research papers [6-11] and review articles[12] have been published on conductive polymers.

Silicone rubber can be blended with other elastomers and plastics like polyethylene. This makes it possible to obtain a sufficiently high electrical conductivity with low filler content owing to the accumulation of carbon black in the phase of one of the polymers. By mixing silicone rubber with polyethylenes, vulcanizates with high electrical conductivity along with good mechanical properties can be prepared. The property of high temperature stability and chemical resistance are maintained in the conducting vulcanizates.

This chapter is divided into three parts; Part-I reports the effect of different types of carbon blacks [e.g., acetylene black, lamp black, and ISAF (N-234) black], copper powder, and graphite on the electrical conductivity and mechanical properties of silicone rubber. Part –II reports the effect of different types of carbon blacks [e.g., N-220, N-347, and N-339 carbon blacks] on the electrical conductivity and mechanical properties of silicone rubber. The effect of temperature on the conductivity of silicone rubber vulcanizates is also studied. Part-III reports the effect of blending silicone rubber with high-density polyethylene on the conductivity and mechanical properties of the vulcanizates.

3. 2 Materials Used

. General purpose silicone rubber, High density polyethylene, Acetylene black, Intermediate Super Abrasion Furnace black [(ISAF) (N-234)], Lamp black, Intermediate Super Abrasion Furnace black (ISAF, N- 220), High Abrasion Furnace black (HAF, N-339 and N-347), Graphite powder, Copper powder, and 40% active dicumyl peroxide (DCP) were used in the present investigation conforming to the specifications given in Chapter 2.

3.3 Part I

Effect Of Carbon Black, Copper Powder And Graphite On Conductivity of Silicone Rubber

3.3.1 Sample Preparation

The compounds as per the formulation given in Table 3.I (a-d) were mixed in a Brabender Plasticorder PL3S with a rotor speed of 50 rpm at room temperature for 6 min. Each batch was then sheeted out by passing through a two roll mill of size (15 x 33 cm), which was convenient for the subsequent preparation of test specimens. The compounds were kept for 24 h for maturation. The optimum cure time (time for attaining 90% of the maximum torque) of each sample was determined at 180^{0}C using Goettfert Elastograph model 67.85.

The compounds were compression moulded at 180^{0}C, in an electrically heated hydraulic press, into 1-mm-thick sheets. For this, the mould was preheated to 180^{0}C, a piece of preformed material was placed directly in the mould cavity, and compressed under an hydraulic clamp pressure of 200 kg cm^{-2}. Upon completion of the required cure cycle, the pressure was released and the sheet was stripped from the mould and suddenly cooled by plunging into cold water. After a few seconds, the samples were taken from the cold water. When the amount of acetylene black and ISAF black was above 40phr, the strength of the sheets were very low and hence the concentration of acetylene black and ISAF black was limited to 40 phr.

Dumbbell shaped test specimens were punched out of these compression-moulded sheets along the mill grain direction. The tensile properties were measured on a Zwick UTM model 1445 using a crosshead speed of 500 mm min^{-1}

according to ASTM D 412. Data presented are average values after testing three samples.

Tear strength of the vulcanizates were measured on the Zwick UTM according to ASTM D 264 using angular test specimens. The hardness (Shore A) of each sample was also noted, according to ASTM D 2240.

Table 3.1 (a) Formulation of compounds

Mix	A_1	A_2	A_3	A_4	A_5
Silicone rubber	100	100	100	100	100
Dicumylperoxide	2.5	2.5	2.5	2.5	2.5
Acetylene black	5	10	20	30	40

Table 3.1 (b) Formulation of compounds

Mix	B_1	B_2	B_3	B_4	B_5	B_6	B_7
Silicone rubber	100	100	100	100	100	100	100
Dicumylperoxide	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Lamp black	5	10	20	30	40	50	60

Table 3.1 (c) Formulation of compounds

Mix	C_1	C_2	C_3	C_4	C_5
Silicone rubber	100	100	100	100	100
Dicumylperoxide	2.5	2.5	2.5	2.5	2.5
ISAF black	5	10	20	30	40

Table 3.1 (d) Formulation of compounds

Mix	D_1	D_2	D_3	D_4	E_1	E_2	E_3	E_4
Silicone rubber	100	100	100	100	100	100	100	100
Dicumylperoxide	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Copper powder	5	15	40	75	25	25	25	25
Graphite powder	-	-	-	-	10	10	10	10
Acetylene black	-	-	-	-	-	10	20	30

Resistivity of each sample was determined using the two-probe method. Data presented are the average of two samples. The samples with typical dimensions of 3 x 1.5 x 0.1 cm^3 were prepared for direct current electrical resistivity measurements. The sample was inserted between two electrodes. The contact resistance between the electrode and the sample was minimized using silver paint. A potential of 6 V was applied, and the resulting current through the circuit was noted at a rotary vacuum of 10^{-2} torr. For high resistivity samples, the resulting current through the circuit was measured using an electrometer amplifier (model no. EA 815). For low resistivity samples, the resulting current was measured using a digital multimeter (APLAB model 1087). Resistance of the samples was calculated using the equation, R= V/I, where 'V' is the applied voltage and 'I' is the resulting current. The resistivity in each case was calculated using the equation, ρ=(RA/t), where 'A' is the area of the sample and 't' is the thickness of the sample. The temperature dependence of resistivity was measured in the temperature range of 25 to 150^0C by raising the temperature at a heating rate of 2^0C min^{-1} and then by slow cooling up to 50^0C. The cooling rate was controlled by adjusting the voltage given to the heating coil. The cooling rate was 1.5^0C min^{-1} up to 75^0C and then it was 1°C min^{-1} up to 50°C. To test the reproducibility of the experimental results, the temperature cycling was repeated for the same test piece.

3. 3 .2 Results and discussion

The cure times of compounds A_1-A_5 decreased as the concentration of acetylene black increased as shown in the figure 3.1. The decrease in cure time may be due to the accelerating effect of acetylene black in silicone rubber. For the compounds B_1-B_7 and C_1-C_5 cure time increased gradually as the concentration of lamp black and ISAF (N-234) black increased as shown in the figure 3.2. This may be due to the retarding effect of lamp black and ISAF black. For compounds D_1-D_4, the cure time increased with increase in the concentration of copper powder as shown in the figure 3.3. For compounds E_1-E_4, the cure time decreased with increasing concentration of acetylene black, similar to those for compounds A_1-A_5 and it is shown in the figure 3.4.

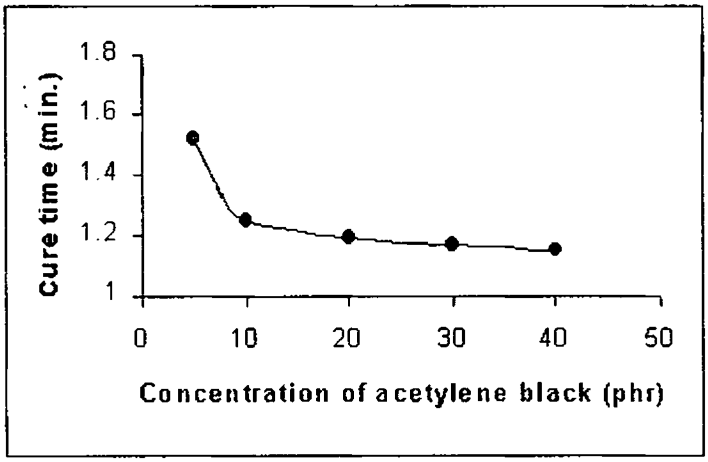

Fig.3.1 Variation in cure time with concentration of acetylene black

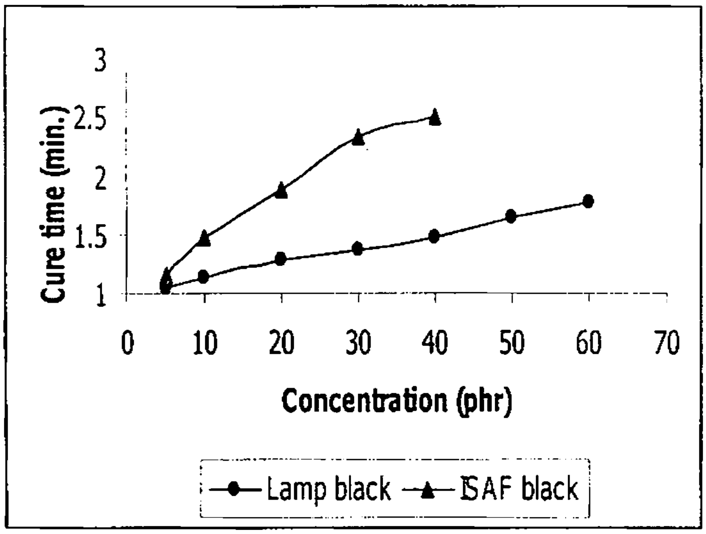

Fig. 3.2 Variation in cure time with concentration of Lamp black and ISAF (N-234) black

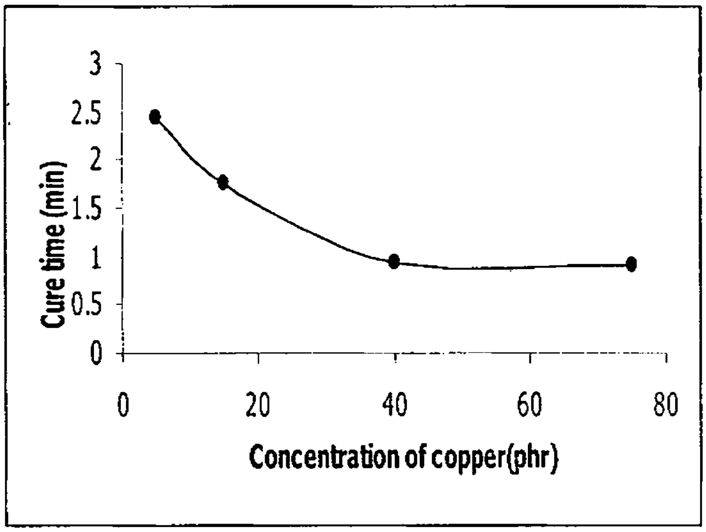

Fig.3.3 Variation in cure time with concentration of copper powder

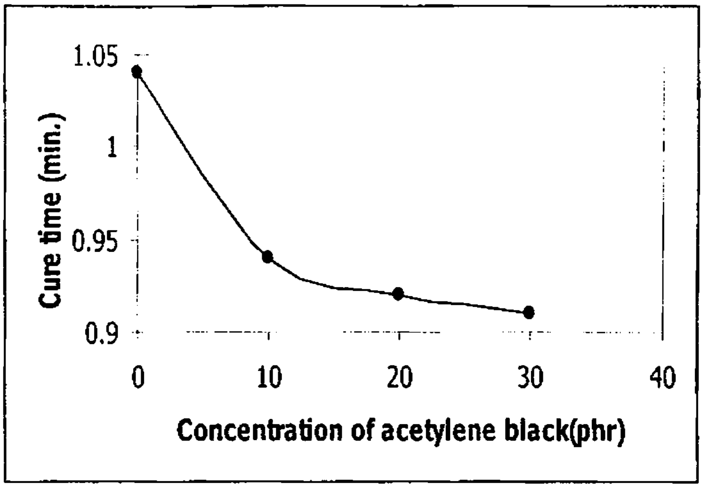

Fig.3.4 Variation in cure time with concentration of acetylene black along with 10 phr graphite and 25 phr copper powder

The variation in the mechanical properties like tensile strength, tensile modulus at 100% elongation, tear strength, elongation at break, and hardness of different vulcanizates are given in the figures 3.5 – 3.19. With increasing the amount of different blacks, tensile strength, tear strength and elongation at break gradually decreased. The decrease in tensile and tear strength was due to the decreasing volume fraction of silicone rubber in the compounds containing a higher concentration of carbon blacks. As the concentration of carbon black increased, there were not enough rubber matrixes to hold the particles of the carbon black; thus the tensile and tear strength was decreased. Elongation at break also decreased with an increase in carbon black loading. The tensile strength, tear strength and elongation at break also decreased with increase in the concentration of copper powder. The reason for this behaviour is the same as that in the case of compounds containing carbon black.

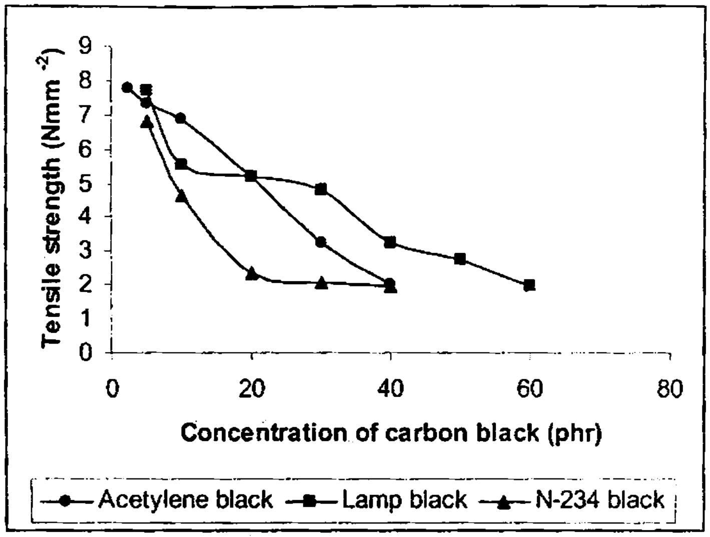

Fig.3.5 Variation in tensile strength.with concentration of different carbon blacks

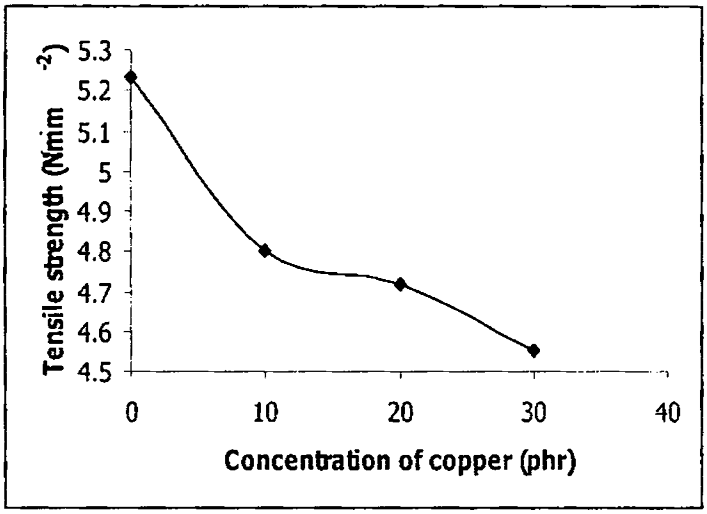

Fig.3.6 Variation in tensile strength with concentration of copper powder

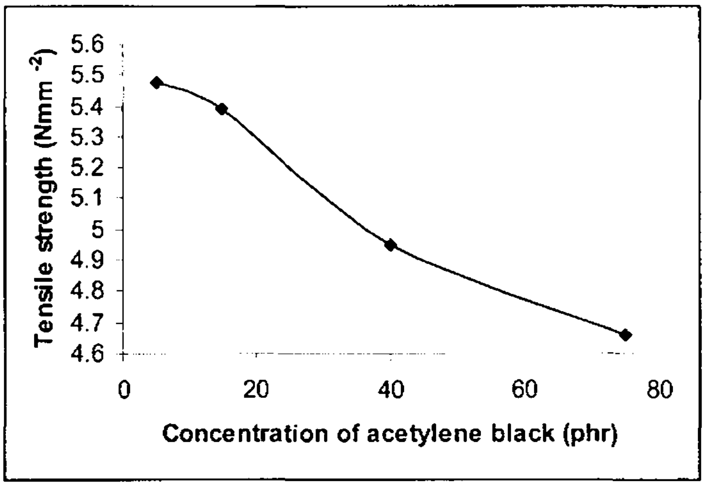

Fig.3.7 Variation in tensile strength with concentration of acetylene black along with 10 phr graphite and 25 phr copper powder

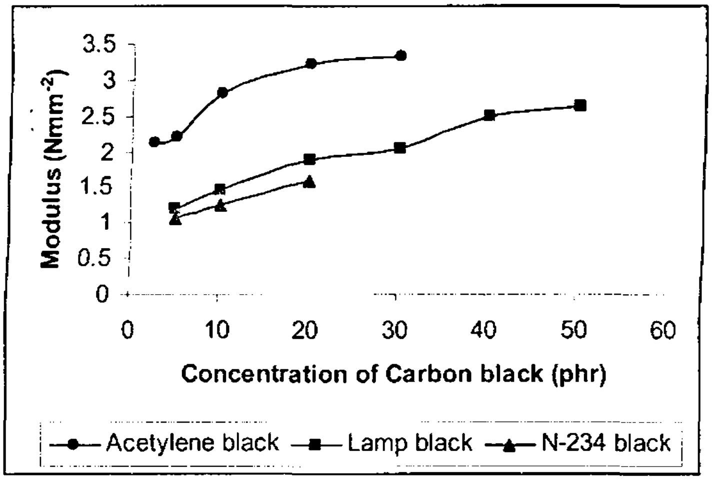

Fig.3.8 Variation in modulus with concentration of different carbon blacks

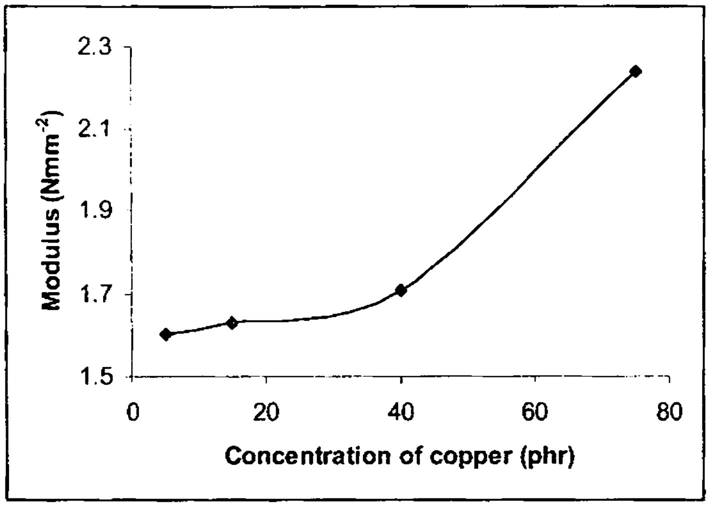

Fig.3.9 Variation in modulus with concentration of copper powder

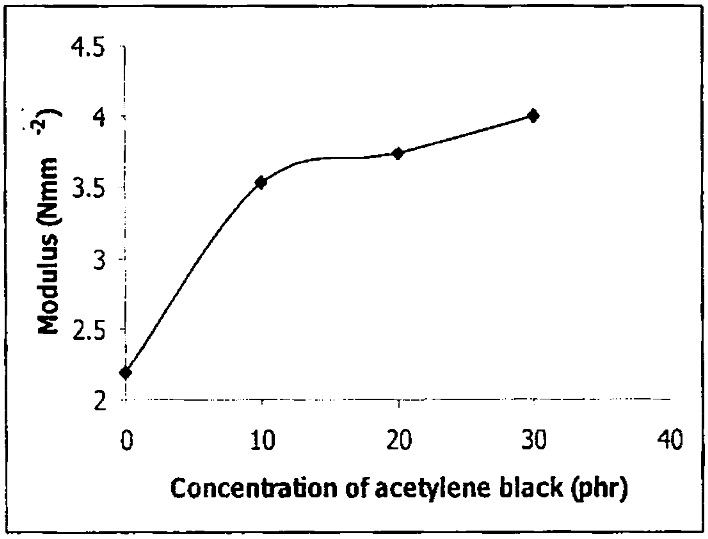

Fig.3.10 Variation in modulus with concentration of acetylene black along with 10 phr graphite and 25 phr copper powder

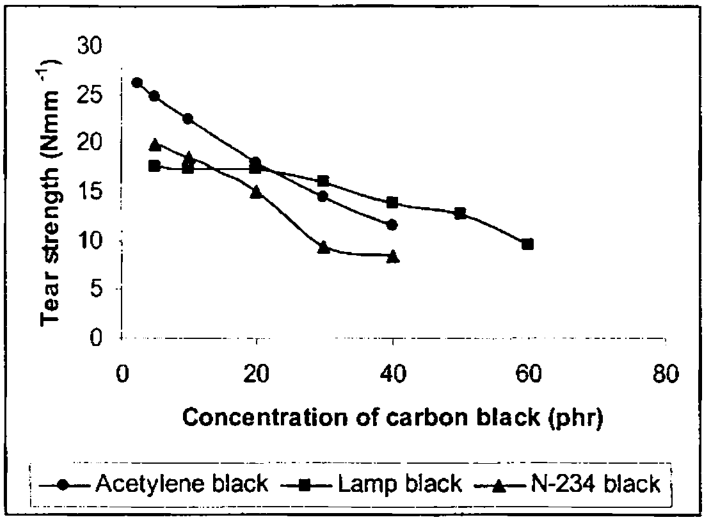

Fig.3.11 Variation in tear strength with concentration of different carbon blacks

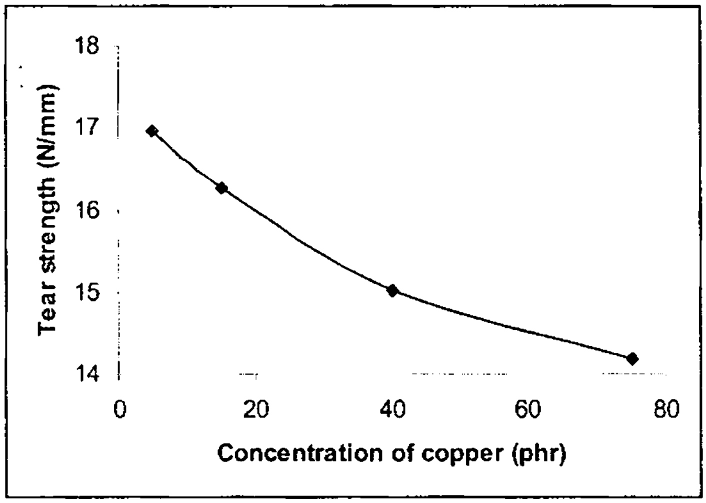

Fig.3.12 Variation in tear strength with concentration of copper powder

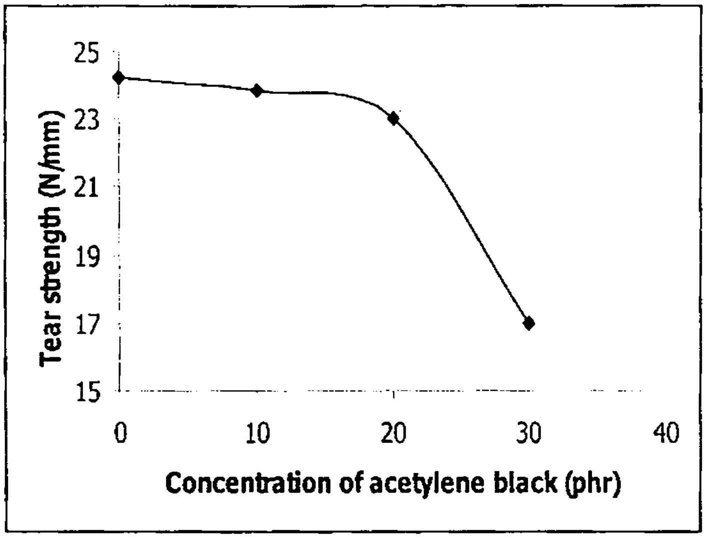

Fig.3.13 Variation in tear strength with concentration of acetylene black along with 10 phr graphite and 25 phr copper powder

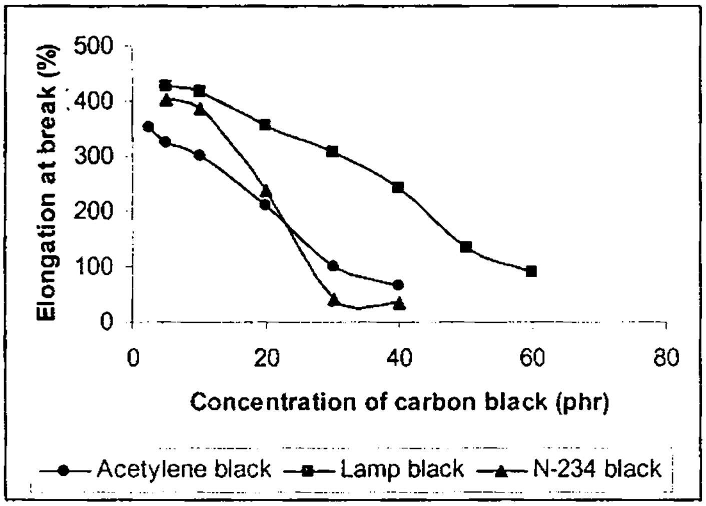

Fig.3.14 Variation in elongation at break with concentration of different carbon blacks

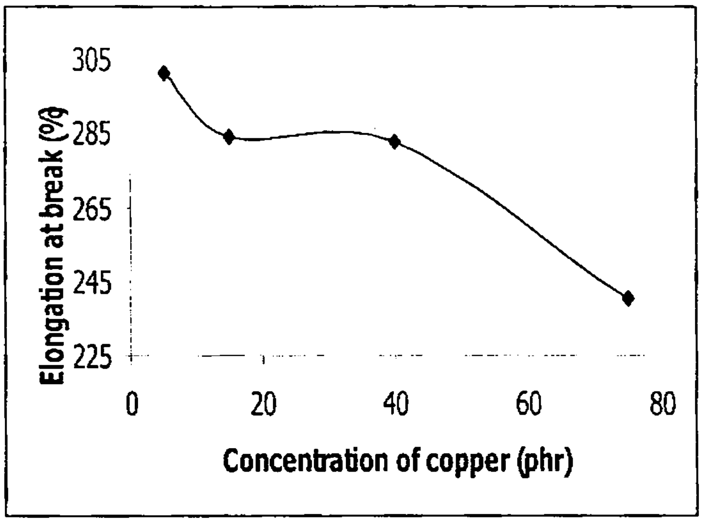

Fig.3.15 Variation in elongation at break with concentration of copper powder

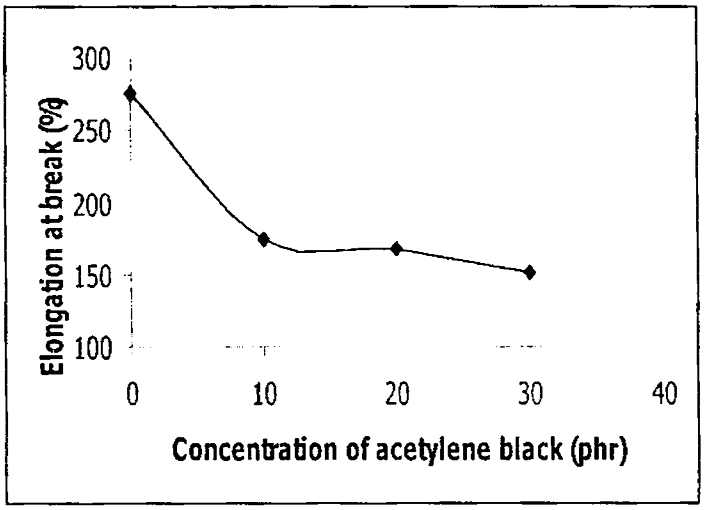

Fig.3.16 Variation in elongation at break with concentration of acetylene black along with 10 phr graphite and 25 phr copper powder

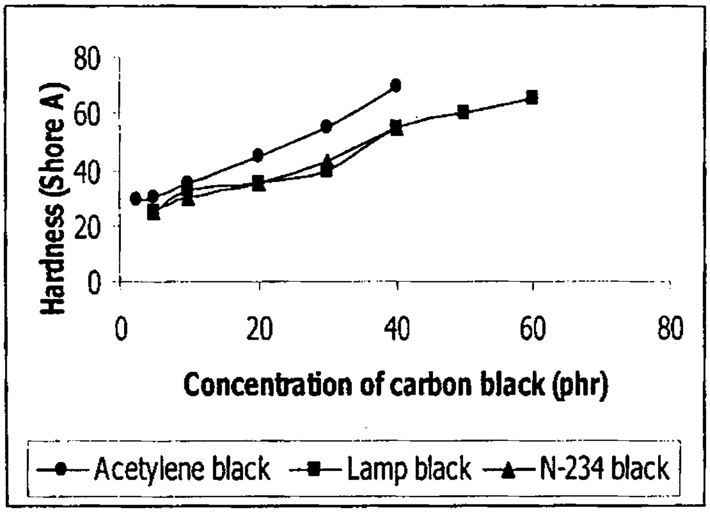

Fig.3.17 Variation in hardness with concentration of different carbon blacks

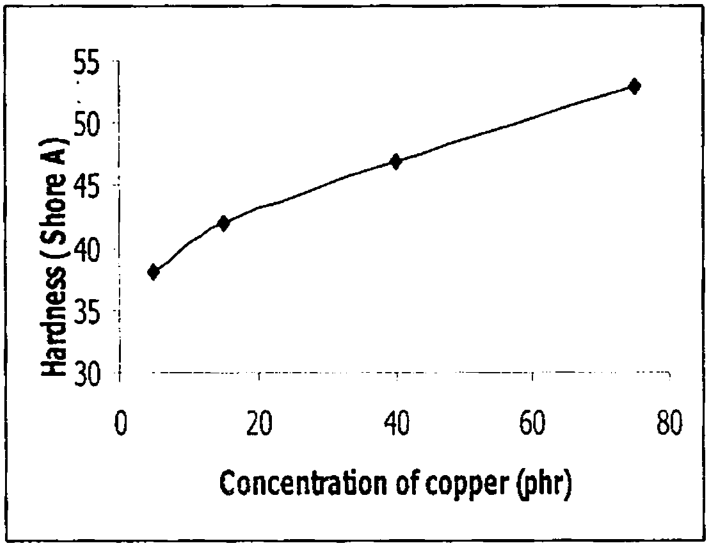

Fig.3.18 Variation in hardness with concentration of copper powder

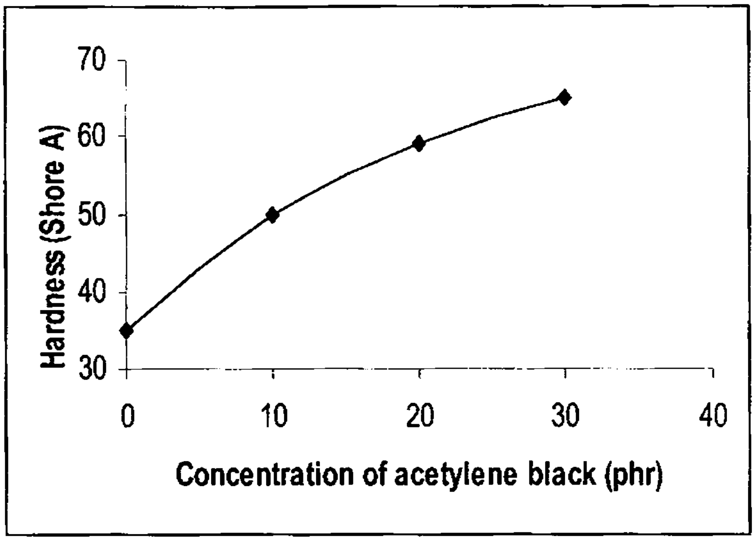

Fig.3.19 Variation in Hardness with concentration of acetylene black along with 10 phr graphite and 25 phr copper powder

Figure 3.20 shows the variation in resistivity of silicone rubber vulcanizates with the concentration of different blacks at room temperature. At low loadings of carbon black, the conductivity of the compounds was very low. This was because the carbon black particles were isolated from each other, and there was no conducting path. As the loading of carbon blacks was increased, the conductivity increased rapidly up to a particular concentration, thereafter, the increase in conductivity was not so rapid. This is because, when the amount of carbon black was increased, cluster or aggregates of carbon blacks were formed and a conducting path was formed. Thus, the internal contact resistance between the aggregates decreased as the loading level increased. Once a high enough loading was reached so that contact resistance between the aggregates was no longer significant and there was no significant increase in conductivity with a further increase in loading.

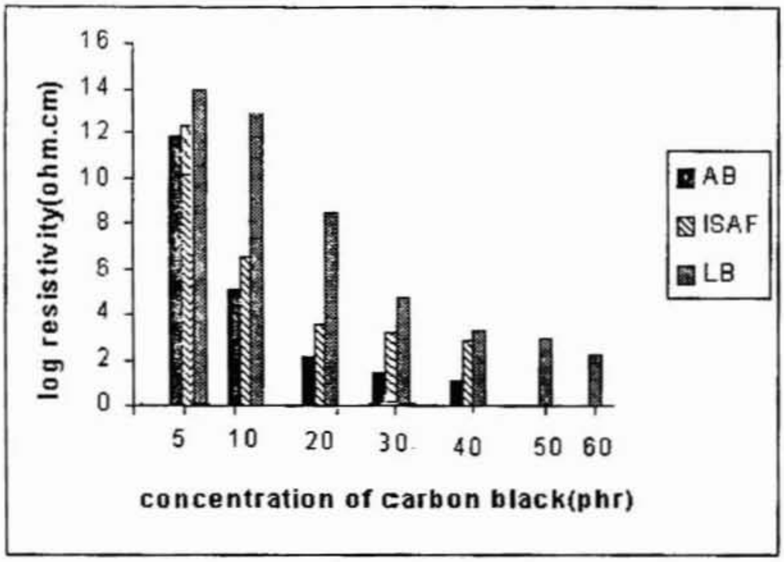

Fig.3.20 Variation in resistivity of silicone rubber compounds with the concentration of different blacks

A comparative electrical conductivity study of the vulcanizates revealed that the conductivity of the vulcanizates filled with acetylene black was higher than that with ISAF black, which had conductivity higher than that of vulcanizates containing lamp black. This behaviour can be explained by considering the very high structure of acetylene black. When acetylene black was added to silicone rubber aggregates of acetylene black comes in contact with each other and a conducting path was easily formed in a concentration range of 10-15 phr by weight. Because the structure of ISAF black was not as high as acetylene black, the compounds filled with ISAF black has lower conductivity, compared with acetylene black. Because lamp black has a still lower structure, the conductivity was low even when a higher amount of lampblack was added.

Figures 3. 21 and 3.22 show the temperature dependence of resistivity for the vulcanizates containing 30 and 40 phr acetylene black, respectively. As the temperature was increased, the conductivity decreased. This behaviour may be due to two factors:

1. The thermal expansion of silicone rubber was higher than that of acetylene black and so the gap width between the aggregates was increased resulting in a decrease in conductivity; and
2. When temperature was increased, some of the aggregates of carbon black break down and so the gap width between the aggregates was increased and so conductivity was decreased.

On cooling, the conductivity was increased. This may be either due to the contraction of silicone rubber so that the gap width decreases or due to the reagglomeration of the particles resulting in gap width decrease and therefore conductivity was increased.[2,10,13]

The nature of the hysteresis loop in the $\rho = f(T)$ curve during the heating-cooling cycle is shown in figure 3.21 and 3.22. It is reported that the hysteresis loop results from the thermal mismatch between filler and polymer.[11,13] The uneven

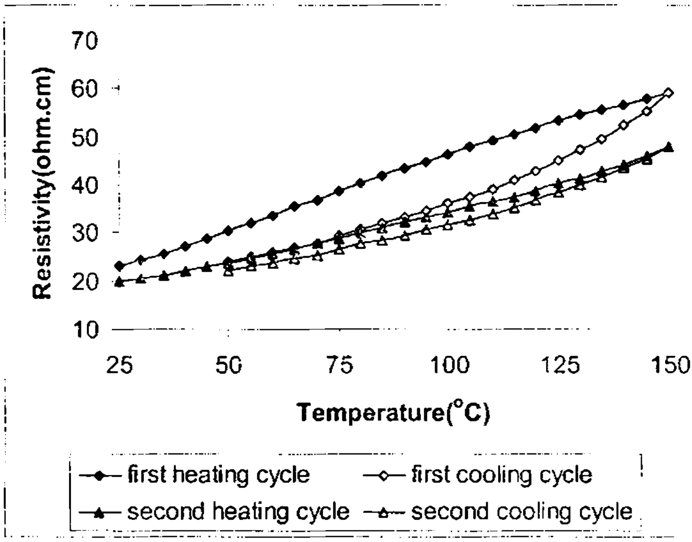

Fig.3.21 Resistivity variation with temperature for silicone rubber vulcanizate containing 30 phr acetylene black

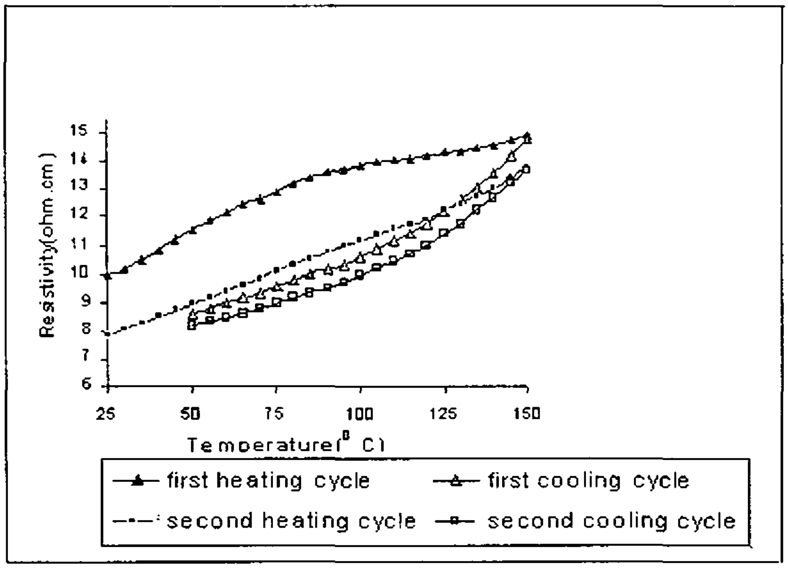

Fig.3.22 Resistivity variation with temperature for silicone rubber vulcanizate containing 40 phr acetylene black

thermal expansion of rubber and acetylene black may be one of the reasons for the creation of a hysteresis loop. Also, during cooling, the size of the aggregates of acetylene black may be greater than that at the heating time. This may be one of the reasons for the higher conductivity on cooling than on heating; thus the hysteresis loop resulted. Also, it has been reported ^{9} that the resistivity of the compound was decreased after heat ageing at 150-250^{0}C and the decrease in resistivity during ageing was explained, due to the increase in the concentration of the carbon black in the system, as a result of a loss of mass (3.8% after 55000 hrs at 150^{0} C). Here also, after heating cycle, ageing of silicone rubber took place, and the conductivity on cooling was higher than on heating; thus, the hysteresis loop was formed.

The resistivity values shown in the graph during the cooling cycle is only up to 50^{0}C, because the cooling rate was very low below 50^{0}C. If we extrapolate the curve to room temperature, the cooling cycle endpoint will be the same as that start point of the second heating cycle. The heating-cooling cycle was repeated for checking the reproducibility of the variation in conductivity with temperature. The nature of the curve was the same, but the area of the hysteresis loop decreased during the second cycle. This was because, some permanent change due to ageing took place for the rubber and a steady state was reached after one cycle.

Figures 3.23 and 3.24 show the temperature dependence of resistivity for vulcanizates containing 40 and 50 phr lamp black, respectively. On heating, the conductivity decreased, due to the thermal expansion of the silicone rubber. This may also be due to the disintegration of lamp black aggregates. On cooling, the conductivity was increased due to the contraction of silicone rubber and may also be due to the reagglomeration of lamp black particles. The overlap of the cooling cycle curves in Figure 3.23 may be due to the same size of the aggregates of lamp black during the cooling process.

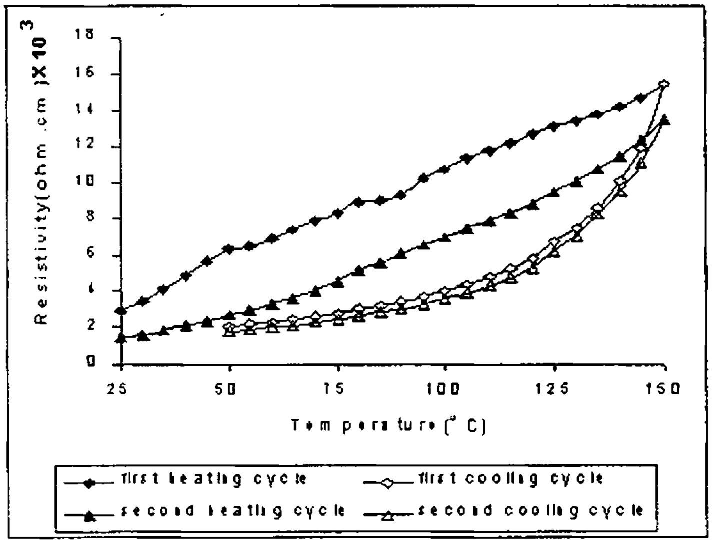

Fig. 3.23 Resistivity variation with temperature for silicone rubber vulcanizate containing 40 phr of Lamp black

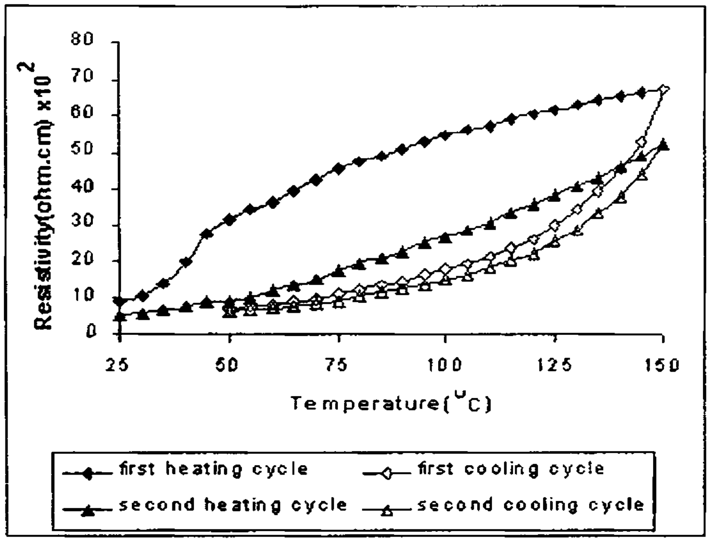

Fig.3.24 Resistivity variation with temperature for silicone rubber vulcanizate containing 50 phr Lamp black

When the concentration of lampblack was increased to 50 phr, overlapping of the cooling curves takes place at a temperature lower than 80^0 C. This may be because the size of the aggregates remained unchanged only at a low temperature.

Figures 3.25 and 3.26 show the temperature dependence of resistivity for the vulcanizates containing 30 and 40 phr ISAF carbon black, respectively. The resistivity was increased on heating up to 80^{0}C. It has been repeatedly observed in several samples that there was an increase in resistivity up to 80^{0}C and then a decrease in its value. A similar observation has been reported earlier by Abo-Hashem and colleagues[10] in butyl rubber mixed with SRF carbon black. They have observed a decrease in conductivity below 60^{0}C for the composites containing 40 and 70 phr SRF; above 60^{0}C, thermally activated behaviour showing an increase in conductivity during the heating cycle was noted.

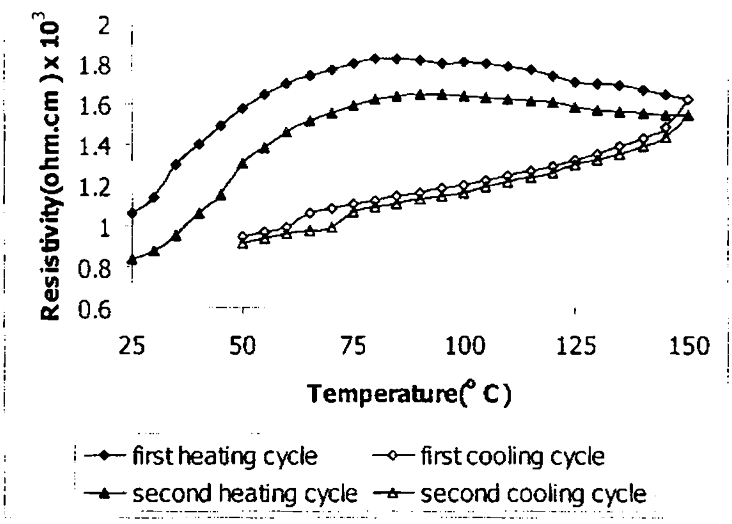

Fig.3.25 Resistivity variation with temperature for silicone rubber vulcanizate containing 30 phr ISAF black

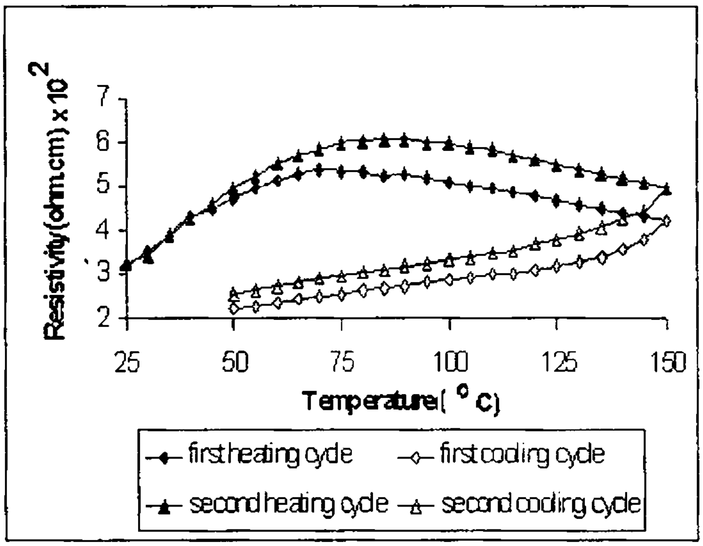

Fig.3.26 Resistivity variation with temperature for silicone rubber vulcanizate containing 40 phr ISAF black

The changes in resistivity during the heating cycle for the compounds containing ISAF black may also be similar to this due to the breakage of the clusters of ISAF black below 80^{0}C and reformation above 80^{0}C. On cooling, only the reformation of ISAF black aggregates takes place and there was no increase in the resistivity versus temperature cooling curve, thus showing that the resistivity was decreased on cooling.

The addition of copper powder and graphite powder into silicone rubber has only very little effect on resistivity as shown in Figure 3.27.The density of copper powder was high compared to that of carbon blacks. So large amount of copper powder was necessary to lower the resistivity of silicone rubber. Also, during vulcanization of silicone rubber, at high temperature, partial oxidation of copper takes place and this also tends to increase the resistivity.

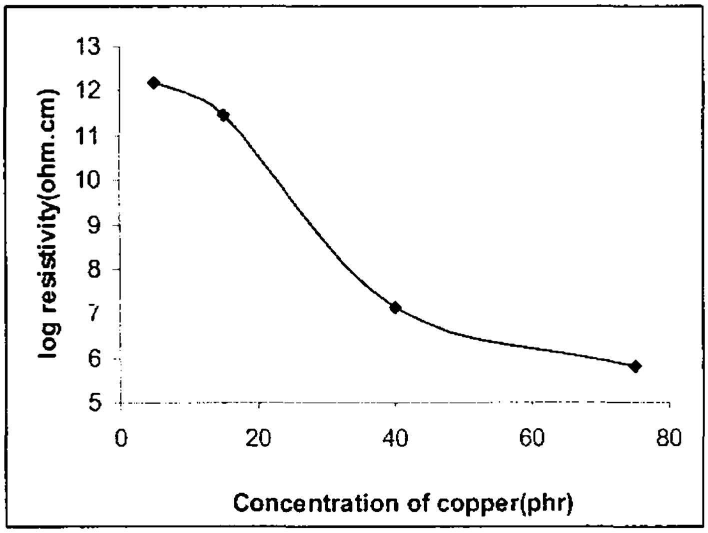

Fig.3. 27 Variation in resistivity of silicone rubber vulcanizates with the amount of copper powder

The effect of addition of copper powder, graphite, and acetylene black on the conductivity of silicone rubber was also studied. The combined effect of these fillers was very low. This was because; carbon black is capable of forming a secondary structure in the form of particle aggregates, which leads to the formation of conducting three-dimensional channels. Even though the conductivity of graphite is more than that of carbon blacks, graphite does not possess this capacity. Composites containing carbon black as the filler are therefore characterized by higher conductivity than composites with an equivalent graphite content. Particles of carbon black with lower electrical conductivity form a secondary structure in the form of bridges between the more conductive graphite particles, thereby including the latter in the overall conducting system[6] in a compound containing both carbon black and graphite. As the amount of acetylene black was increased, resistivity decreased as shown in the figure 3.28.

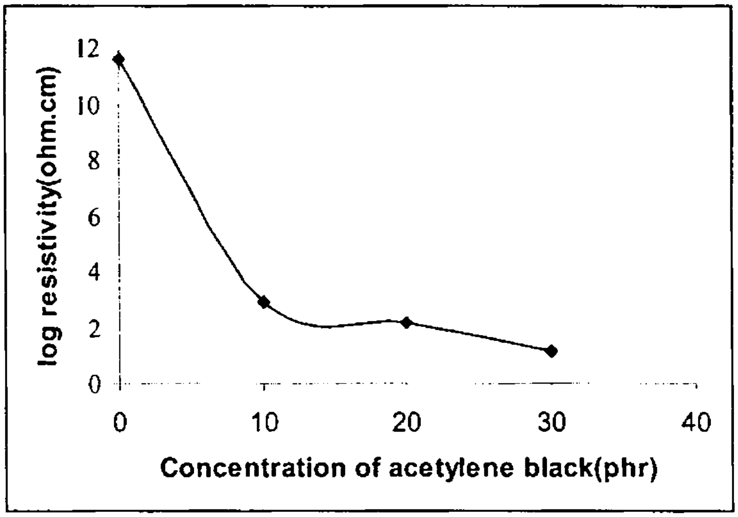

Fig.3. 28 Variation in resistivity of silicone rubber compounds containing 25 phr copper powder and 10 phr of graphite with the concentration of acetylene black

The temperature dependence of resistivity of these vulcanizates was also noted. Figures 3.29 and 3.30 show the temperature dependence of resistivity for vulcanizates containing 20 and 30 phr of acetylene black, along with 25 phr of copper powder and 10 phr of graphite powder. The nature of the curve was similar to that of composites containing acetylene black alone. The conductivity of the vulcanizates was decreased with increase of temperature on heating and the conductivity was increased with decreasing temperature on cooling.

Figure 3.31 shows the variation in the resistivity of silicone rubber vulcanizates containing copper powder and 15 phr acetylene black with temperature. The nature of the curve is similar to that of composites containing acetylene black alone. On heating, the resistivity was increased, due to the thermal expansion of the silicone rubber. This may also be due to the disintegration of acetylene black aggregates. On cooling, the resistivity was decreased due to the contraction of silicone rubber and may also be due to the reagglomeration of acetylene black particles. The addition of copper powder has very little effect on the resistivity of the vulcanizates. This may be due to the oxidation of the copper during vulcanization.

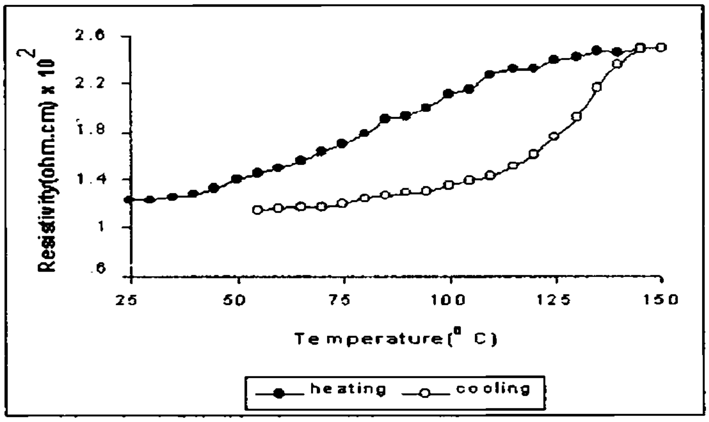

Fig.3.29 Resistivity variation with temperature for silicone rubber vulcanizate containing 20 phr of acetylene black, 25 phr of copper powder and 10 phr of graphite powder.

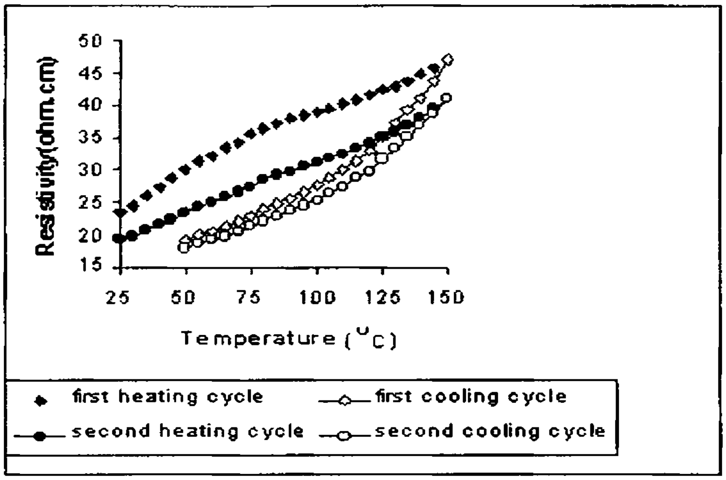

Fig.3.30 Resistivity variation with temperature for silicone rubber vulcanizate containing 30 phr of acetylene black, 25 phr of copper powder and 10 phr of graphite powder.

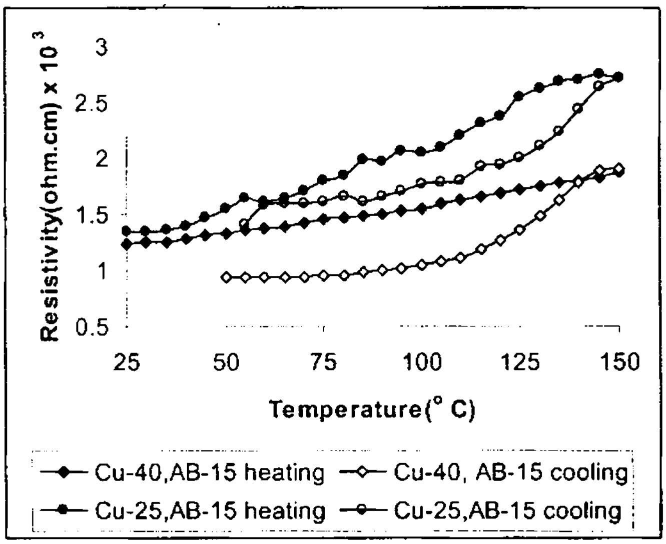

Fig.3.31 Resistivity variation with temperature for silicone rubber vulcanizate containing 15 phr of acetylene black, and 25 phr of copper powder and 40 phr of copper powder.

3.4 PART-II

Effect Of Addition Of Different Carbon Blacks In Silicone Rubber

In this section, the effect of addition of different carbon blacks like ISAF N- 220 black, HAF N-339 black, and HAF N-347 black on the electrical conductivity and mechanical properties of silicone rubber is reported. The influence of temperature on the conductivity of silicone rubber vulcanizates containing different types of carbon black was also studied.

3.4.1 Sample preparation

The compounds as per the formulation given in Table 3.2 were mixed in a Brabender Plasticorder PL3S with a rotor speed of 50 rpm at room temperature for 6 min.

Table 3.2 (a) Formulation of compounds

Mix	H_1	H_2	H_3	H_4	I_1	I_2	I_3	I_4
Silicone rubber	100	100	100	100	100	100	100	100
Dicumylperoxide	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
N-220 black	10	20	30	40	-	-	-	-
N-339 black	-	-	-	-	10	20	30	40

Table 3.2 (b) Formulation of compounds

Mix	J_1	J_2	J_3	J_4
Silicone rubber	100	100	100	100
Dicumylperoxide	2.5	2.5	2.5	2.5
N-347 black	10	20	30	40

3.4.2 Results and discussion

For these compounds, the cure time was increased gradually as the concentration of carbon blacks was increased as shown in figure 3.32. This may be due to the retarding effect of carbon blacks in silicone rubber. Figure 3. 33 show the variation in resistivity of silicone rubber vulcanizates with the concentration of carbon blacks like N- 220 black, N-339 black, and N-347 black at room temperature.

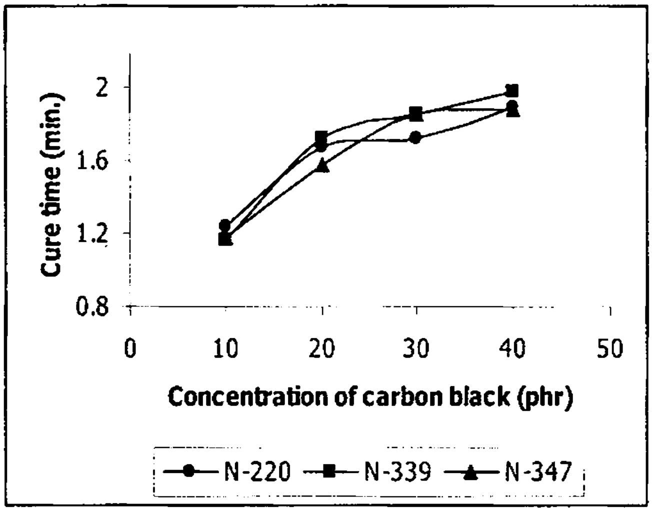

Fig.3.32 Variation in cure time with concentration of carbon black

At low loadings of carbon black, the conductivity of the compounds was very low. This was because the carbon black particles were isolated from each other, and there was no conducting path. As the loading of carbon blacks was increased, the conductivity increased rapidly up to a particular concentration region; thereafter, the increase in conductivity was not so rapid. This was because, when the amount of carbon black was increased, cluster or aggregates of carbon blacks were formed and a conducting path was formed. Thus, the internal contact resistance between the aggregates decreased as the loading level increased. Once a high enough loading was reached so that contact resistance between the aggregates was no longer significant and there was not any significant increase in conductivity with a further increase in loading.

A comparative electrical conductivity study of the compounds revealed that the conductivity of the vulcanizates filled with N-220 black was higher than that with N-347 black, and N-339 black. This behaviour can be explained by considering the smaller particle size of N-220 black compared to the particle size of N-347 black and N-339 black. The conductivity was decreased with increasing particle size of the carbon black. It has been argued [3] on purely geometric grounds that smaller particle size should lead to smaller gap width. It has also been argued[2] that smaller particle size leads to more conducting paths per unit volume. It has also been suggested that[2] the smaller particles arrange themselves more easily into chains than do the coarser types. The particle size of N-347 carbon black and

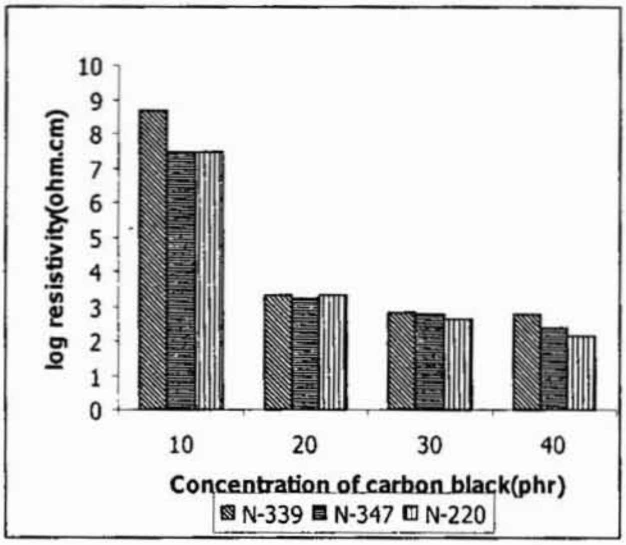

Fig. 3.33 Variation in resistivity of silicone rubber vulcanizates with amount of carbon black

N-339 carbon black is almost the same and hence their conductivity values were almost the same in silicone rubber vulcanizates. The conductivity of the vulcanizates increased rapidly with the addition of carbon blacks initially up to about 20 phr of carbon blacks and thereafter the increase in conductivity with the addition of carbon blacks was very slow. It was because; a through going conducting path was already formed. Once a high enough loading was reached so that contact resistance between the aggregates was no longer significant and there was not any significant increase in conductivity with a further increase in loading.

Properties of the mixes loaded with different types of carbon blacks, like N-220, N-339 and N-347 are given in Table 3.3

Table 3.3 Properties of the vulcanizates

Mix No.	Tensile strength (Nmm^{-2})	Modulus at 100% Elongation (Nmm^{-2})	Modulus at 200% Elongation (Nmm^{-2})	Hardness (Shore A)	Tear strength (Nmm^{-1})	Elongation at break (%)
H_1	9.66	2.10	4.17	35	12.6	391.31
H_2	4.38	1.73	3.22	40	17.59	305.32
H_3	0.9	-	-	50	11.77	36.36
H_4	-	-	-	57	-	-
I_1	7.92	2.42	5.71	45	20.35	308.98
I_2	6.95	2.35	4.05	50	18.62	259.22
I_3	3.82	2.27	-	55	13.97	183.55
I_4	-	-	-	59	-	-
J_1	7.3	2.02	3.99	30	7.67	319.78
J_2	5.43	1.69	3.03	40	15.23	297.52
J_3	2.5	0.86	-	49	13.72	164.61
J_4	-	-	-	53	-	-

The tensile strength and modulus of the vulcanizates was decreased with an increase in the concentration of carbon blacks. The decrease in tensile strength was due to the decreasing volume fraction of silicone rubber in the vulcanizates. As the concentration of carbon black was increased, there were not enough rubber matrixes to hold the particles of the carbon black together. The hardness of the vulcanizates was increased with an increase in the concentration of carbon black.

Tear strength and elongation at break of the vulcanizates were increased initially up to a concentration of 20 phr of carbon black and then decreased with an increase in carbon black loading. It was because, small amounts of carbon black acts as a reinforcing filler and when the amount of carbon black was increased above 20 phr, there was not enough rubber matrix to hold the particles together and the tear strength was decreased.

Figures 3.34 - 3.36 show the variation in the resistivity of silicone rubber vulcanizates with temperature (25- 150 °C), filled with 40 phr of N-220, N-347 and N-339 carbon black respectively. .

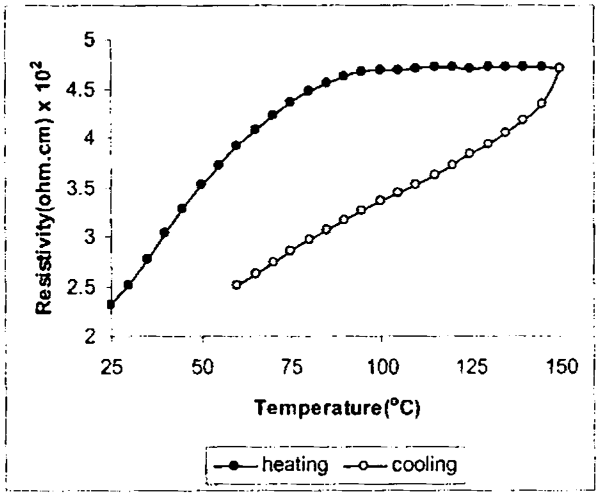

Fig. 3.34 Variation in resistivity with temperature, of silicone rubber vulcanizates with 40 phr of N-220 carbon black

As the temperature was increased, the resistivity was increased. This behaviour may be due to the thermal expansion of silicone rubber and also, some of the aggregates of carbon black break down, so that the gap width between the carbon black aggregates was increased resulting in an increase in resistivity, On cooling, reagglomeration of the particles takes place, the gap width was decreased, and the resistivity was decreased. During cooling, the size of the aggregates of acetylene black may be greater than that at the heating time. This may be one of the reasons for the lower resistivity on cooling than on heating; thus the hysteresis loop was resulted.

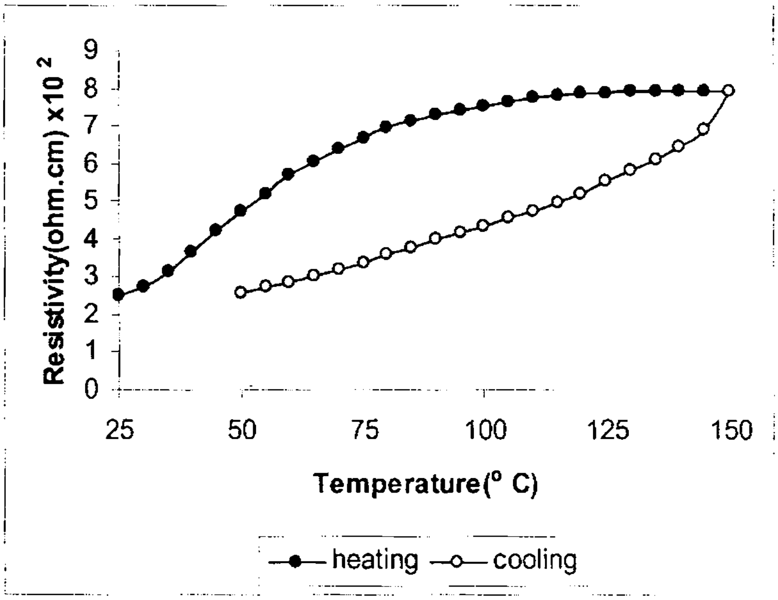

Fig. 3.35 Variation in the resistivity of silicone rubber vulcanizates with temperature, filled with 40 phr of N-347 carbon black

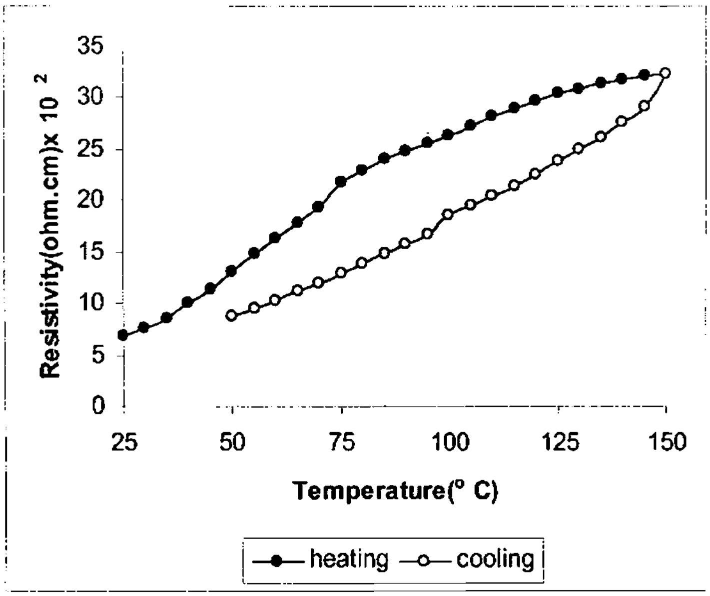

Fig. 3.36 Variation in the resistivity of silicone rubber vulcanizates with temperature, filled with 40 phr of N-339 carbon black

3.5 PART-III

Conductive Silicone Rubber /HDPE Blends

3.5.1 Sample preparation

The compounds as per the formulation given in Table 3.4 were mixed in a Brabender Plasticorder PL3S at a rotor speed of 50 rpm and temperature of 160°C. HDPE was first added, and allowed to melt and homogenize for 2 minutes, the silicone rubber was added and allowed to mix well with HDPE for 2 minutes. 30 phr of acetylene black was added slowly. After adding the acetylene black completely, the mixing was continued for 10 minutes more. Finally, DCP was added and the compound was taken out from the Brabender. The compounds were kept for 24 hrs for maturation.

Table 3.4 Formulation of compounds

Mix	K_1	K_2	K_3	K_4	K_5	K_6	K_7
SR	100	80	70	50	30	20	-
HDPE	-	20	30	50	70	80	100
AB	30	30	30	30	30	30	30
DCP	2.5	2.5	2.5	2.5	2.5	2.5	2.5

The compounds were compression moulded at 180°C, in an electrically heated hydraulic press, into 1-mm-thick sheets. For this, the mould was preheated to 180°C, a piece of preformed material was placed directly in the mould cavity, and compressed under an hydraulic clamp pressure of 200 kg cm^{-2}. After 10 minutes, the mould was allowed to cool to room temperature and then the mould was opened and the samples were taken out.

3.5.2 Results and discussion

The variation in the resistivity of different silicone rubber/HDPE blends containing 30 phr of acetylene black is shown in Fig.3.37. SR/HDPE blends had more conductivity than pure silicone rubber vulcanizate at the same dosage of acetylene black (30phr). This behaviour can be explained by the difference in the dispersion of acetylene black in different phases as well as in the interphase. Blends always have more conductivity compared to the individual polymer. This was due to the selective localization of acetylene black in one phase or at the interphase of the polymer matrix[14]. 70/30 SR/HDPE blends had the lowest resistivity among the different SR/HDPE blends. This can be explained by the difference in the interaction of polymer and acetylene black. 70/30 SR/HDPE blends may have the maximum phase separation, and therefore the acetylene black aggregates may be formed in the interphase of silicone rubber and HDPE. So conducting paths were easily formed and hence the conductivity was increased.

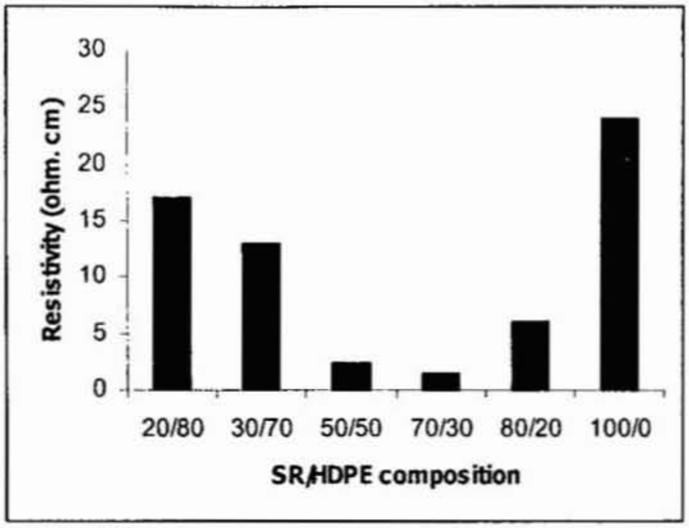

Fig. 3.37 The variation in the conductivity of different SR/HDPE blends containing 30 phr of acetylene black

Starting from left to right, resistivity decreased with increase in the amount of silicone rubber until it reached a minimum, and then it was found to be increasing, probably at the point of reversal of continuous phase[15,16]. Initially acetylene black was dispersed in silicone rubber. When the amount of HDPE increases, the phase separation increases, and the AB gets dispersed at the interphase and hence resistivity decreased. At 70/30 SR/HDPE compositions, there was maximum phase separation. After that, the continuous phase changes to HDPE. Then there was redistribution of AB and the resistivity was increased.

The variation in tensile strength and elongation at break of different SR/HDPE blends are shown in the figures 3.38 and 3.39. Tensile strength of the blends was decreased with increase in the amount of silicone rubber. This was because, HDPE, which is a thermoplastic material can improve the strength of a vulcanizate. Elongation at break of the blends was increased on increasing the amount of silicone rubber, due to its increase in elastic nature.

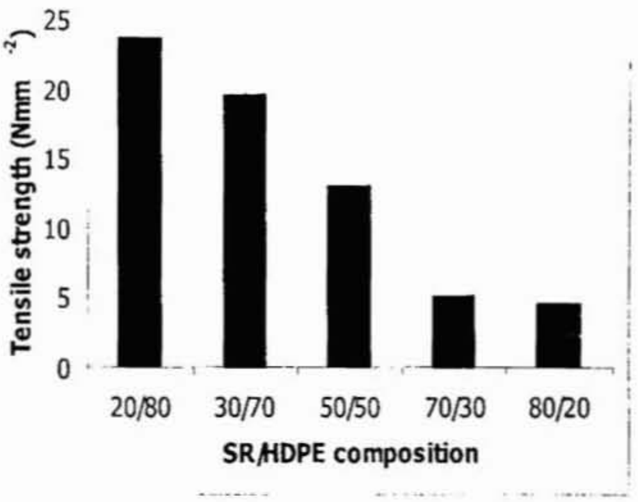

Fig. 3.38 The variation in tensile strength of different SR/HDPE blends containing 30 phr of acetylene black

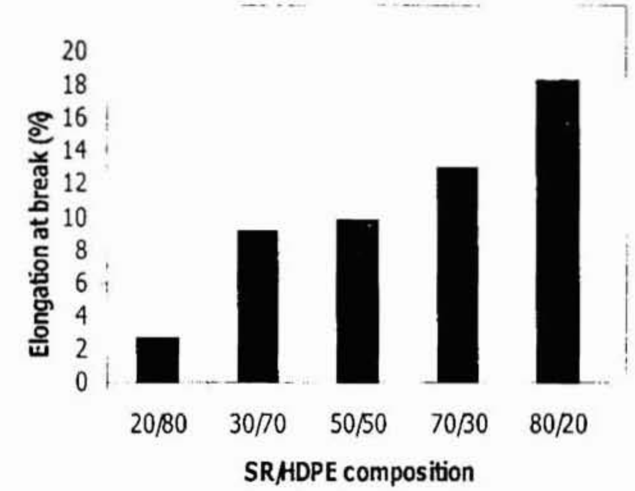

Fig. 3.39 The variation in elongation at break of different SR/HDPE blends containing 30 phr of acetylene black

3. 6 Conclusions

The following conclusions can be drawn from this investigation.

1. The resistivity of the vulcanizates that contain carbon blacks and other conductive fillers like acetylene black, lamp black, ISAF black, N-220 black, N-339 black, N-347 black, copper powder, graphite etc. was decreased as the concentration of carbon blacks and other conductive fillers was increased.
2. The mechanical properties like tensile strength, tear strength and elongation at break were decreased, while hardness was increased as the amount of conductive fillers increased.
3. Resistivity of the silicone rubber vulcanizates was increased on heating but decreased on cooling in the case of all conductive fillers except ISAF black (N-247). For ISAF black, resistivity was first increased, reached a maximum at 80^{0}C, and then decreased on heating.
4. The area of the hysteresis loop during the heating-cooling cycle depends on the carbon black concentration.
5. The conductivity of silicone rubber vulcanizates containing acetylene black was higher than that of other vulcanizates filled with other conductive fillers.
6. The conductivity of SR/HDPE blends was higher than that of pure silicone rubber vulcanizates.
7. 70/30 SR/HDPE blends show the least resistivity among the different SR/HDPE blends.
8. The tensile strength of the SR/HDPE blend was higher than that of pure silicone rubber vulcanizates.

3.7 References

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Chapter 4

DEVELOPMENT OF CONDUCTIVE NITRILE RUBBER

4.1 Introduction

Nitrile rubber, a copolymer of butadiene and acrylonitrile has good resistance to a wide variety of oils and solvents and hence is widely used in products like oil seals, pipe protectors and blow out preventors etc. The acrylonitrile (ACN) content varies usually from 20-50% by weight and accordingly NBR is usually classified into three types, viz., low acrylonitrile content NBR with less than 25%, medium with 25-35 % and high acrylonitrile content NBR with 35-50 %. NBR gives low gum strength, as there is no crystallinity in the polymer. The service temperature in presence of oxygen is estimated to be 130°C.

Major properties of the elastomer depend on the acrylonitrile content. As the acrylonitrile content increases, the oil resistance increases. Other properties affected by monomer ratio are processability, cure rate, heat resistance, and resistance to permanent set. With increased acrylonitrile content, processability is easier, cure rate is faster and heat resistance is better[1]. But, resistance to permanent set and die swell is decreased, and viscosity is increased as the acrylonitrile content increases.

The most common way to classify nitrile rubbers is by their bound acrylonitrile content, and by their viscosity. The bound acrylonitrile content as described above goes from about 20 - 50 % with the bulk as 25 - 40 % range. Mooney viscosity ordinarily ranges from 30 - 80.

Basically nitrile rubbers are compounded much like natural rubber. Since it does not crystallise, reinforcing fillers are necessary to obtain reasonable tensile, tear and abrasion properties. In black compounds, reinforcement is proportional to the amount and fineness of the black. Non-black fillers give best heat resistance and also can be used with compound used for food contact applications.

Fine precipitated silica is the most reinforcing among the non-black fillers. Plasticizers are used in almost all nitrile compounds first to aid processing and then to improve low temperature flexibility, resilience, and flexing, or to reduce hardness. Plasticizer level will ordinarily vary from 5 - 50 phr.

Nitrile rubber requires age resistors in addition to those they already have in order to give long service. Where staining is not a problem, amine type antioxidants may be used. If staining is objectionable, then phosphates or hindered phenol antioxidants will serve better.

Vulcanization of nitrile rubber is usually accomplished with sulphur, accelerator, and ZnO in combination with fatty acid as activator. In special cases, peroxide may also be used. NBR cures relatively fast, the higher acrylonitrile content, faster the cure rate. The amount of sulphur used is based on butadiene content and is generally lower than that used for natural rubber and ranges from 0.7-2.3 phr. The solubility of sulphur is considerably less and affect it's uniform dispersion, for this reason, sulphur is added early in the mix.

Because of the relatively fast rate of cure, NBR is usually compounded with one accelerator, often of the sulphenamide class. Accelerator of the thiazole type like tetramethylthiuram monosulfide (TMTM) or tetramethylthiuram disulfide (TMTD) might be used when a faster curing is needed.

Electrically conductive polymer composites are widely used in various branches of engineering in many rubber and plastic products. Some of these applications include plastic batteries, sensors, electro chromic displays, EMI shielding, fuel cells, circuit boards etc[2]. The basic and generally accepted concepts of conductivity are based on the fact that carbon black forms aggregates or network structures in the compositions[3-5]. The degree of conductivity depends on the nature of these chain structures. In recent years papers relating to the effect of various factors influencing the conductivity of polymer compositions containing carbon black have been published- like type of carbon black [3,4], concentration of carbon black[4,5], type of polymer[6], temperature[4,7] and degree of dispersion of carbon black in the polymer matrix[8,9]. It is shown that starting at a certain level, an increase in the amount of carbon black in a composition leads to a marked increase in conductivity and this then tends asymptotically to a finite value.

The amount of electrically conductive fillers required to impart high conductivity to an insulating polymer can be dramatically decreased by the selective localization of the filler in one of the phase or at the interphase of a polymer blend [8,9]. Not only the final cost of the material is decreased, but the problems associated with the excess of filler on the processing and mechanical properties of the final composites are alleviated. The localization of carbon black in an immiscible polymer blend is basically controlled by the mutual polymer-polymer and polymer –filler interaction [10,11].

This chapter is divided into four parts; Part I deals with the effect of concentration of acetylene black on the electrical conductivity and mechanical properties of nitrile rubber vulcanizates. Part II deals with the effect of blending of

NBR with other polymers on the electrical conductivity and mechanical properties of the vulcanizates at the same dosage of acetylene black. Nitrile rubber blends with NR, EPDM and PVC was prepared and the electrical conductivity and mechanical properties are reported. Part III deals with the variation in conductivity and mechanical properties of the vulcanizates with different composition of NBR/NR blends at the same dosage of acetylene black. Part –IV deals with the effect of temperature on the electrical conductivity of these vulcanizates.

4.2 Experimental

4.2.1 Materials Used

Nitrile rubber (NBR), Natural rubber (NR), Polyvinylchloride (PVC), Ethylene –propylene-diene rubber (EPDM), Acetylene black (AB), Zinc oxide (ZnO), Magnesium oxide (MgO), Stearic acid (SA), Dibenzthiazyldisulphide (MBTS), Sulphur , Tetramethylthiuramdisulphide (TMTD), and Dioctylphthalate (DOP) conforming to the specifications given in Chapter 2 were used in the present investigation.

4.3 Part-I Studies On Conductive Nitrile Rubber

4.3.1 Sample Preparation

The compounds were prepared as per the formulation given in Table- 4.1 on a two-roll mill of size (15 x 33 cm). The compounds were kept for 24 hrs. for maturation.

The optimum cure time (time for attaining 90% of the maximum torque) of each sample was determined at 150^{0}C using Goettfert Elastograph Model 67.85

The compounds were compression molded at 150°C in an electrically heated hydraulic press, into 2mm thick sheets. For this, the mould was pre-heated to 150 °C; a piece of preformed material was placed directly in the mould cavity, and compressed under a hydraulic pressure of 200 Kgcm^{-2}. Upon completion of the required cure cycle, the pressure was released and the sheet was stripped off from the mould and suddenly cooled by plunging into cold water. After a few seconds, the samples were taken from water. Dumb-bell shaped specimens were punched out of these compression-moulded sheets along the mill grain direction. The tensile properties were measured on a Zwick UTM model 1445 according to ASTM D 412 at a crosshead speed of 500 mm/min. The values presented are the average of three samples.

Table 4.1 Formulation of compounds

Mix	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	A_{11}
NBR	100	100	100	100	100	100	100	100	100	100	100
AB	0	10	20	30	40	50	60	70	80	90	100
ZnO	4	4	4	4	4	4	4	4	4	4	4
SA	2	2	2	2	2	2	2	2	2	2	2
S	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
MBTS	1	1	1	1	1	1	1	1	1	1	1
TMTD	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
DOP	-	1	2	3	4	5	6	7	8	9	10

The Hardness (Shore-A) of each sample was noted according to ASTM D 2240. Resistivity of each sample was determined using two- probe method. Data presented are the average of three samples. The samples with typical dimensions of 3x1x2 cm were prepared for direct current electrical conductivity measurements. The sample was inserted between two electrodes. The contact resistance between the sample and the electrode was minimized using silver paint. A potential of 6 V was applied and the resulting current through the circuit was noted. Measurements were carried at a rotary vacuum of 10^{-2} torr. The current was measured using a digital multimeter (APLAB model 1087). Resistance of the samples were calculated using the equation, R= V/I. where, 'V' is the applied voltage and 'I' is the resulting current. The resistivity in each sample was calculated using the equation, ρ =R A/t, where 'A' is the area of the sample, and 't' is the thickness of the sample. Conductivity is the reciprocal of resistivity.

4.3.2 Results and discussion

Figures 4.1- 4.5 shows the physical properties of the vulcanizates. It was found that cure time of the compounds was decreased as the amount of acetylene black increased as shown in Figure 4.1 because of the accelerating effect of acetylene black on vulcanization, up to about 60 phr of acetylene black. Above 60 phr, the change in cure time with the concentration of acetylene black was negligible and it remained almost constant.

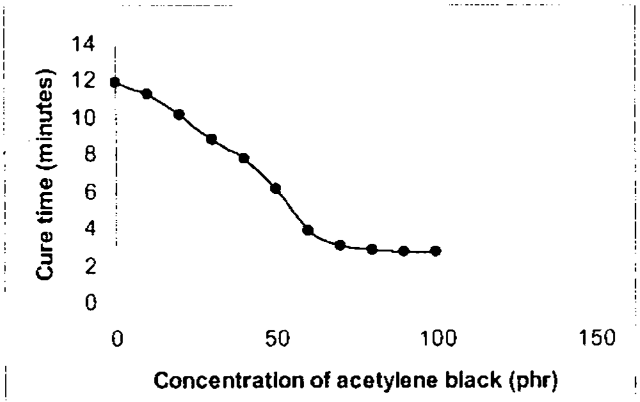

Fig.4.1 Variation in cure time of the compounds of NBR Containing different amounts of acetylene black

Hardness (Shore-A) of the compounds increased with an increase in the concentration of acetylene black. But above 60 phr of acetylene black, the change in hardness with increase in the amount of acetylene black was negligible. This was because, a saturation point was reached at a concentration of 60 phr of acetylene black as shown in Figure 4.2. Figure 4.3 shows the variation in elongation at break of the vulcanizates containing different amounts of acetylene black. Elongation at break decreased with an increase in the amount of acetylene black as expected up to about 60 phr of acetylene black and thereafter it remained almost as constant.

Tensile strength of the vulcanizates was increased as the concentration of acetylene black increased as shown in the Figure 4.4. It was because; acetylene black was acting as reinforcing filler in nitrile rubber.

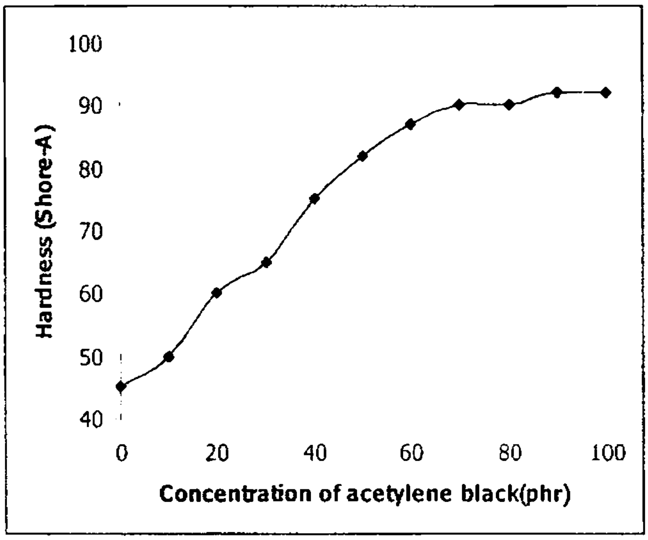

Fig. 4.2 Variation in hardness of vulcanizates with the amount of acetylene black

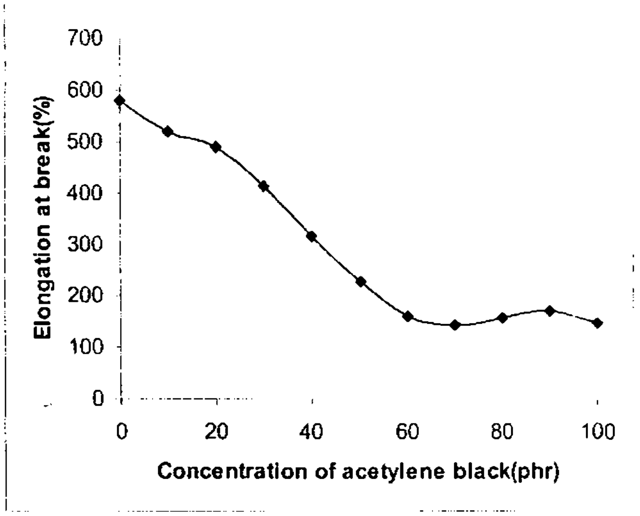

Fig. 4.3 Variation in elongation at break of vulcanizates with the amount of acetylene black

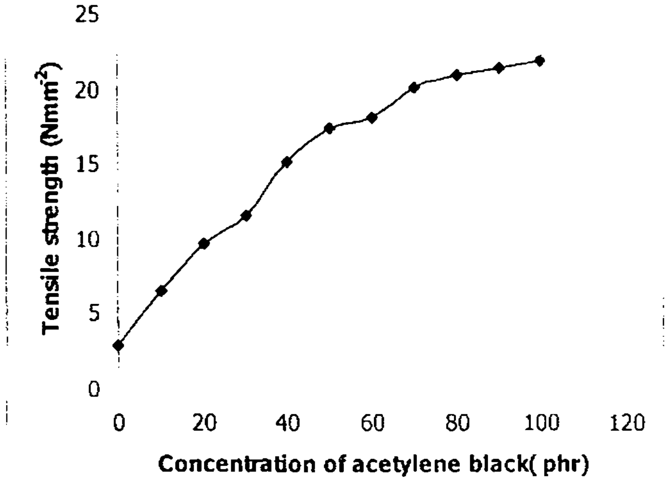

Fig. 4.4 Variation in tensile strength of vulcanizates with the amount of acetylene black

As the amount of acetylene black was increased, the modulus of the vulcanizates increased as shown in the figure 4.5. As the amount of acetylene black was increased, the conductivity of the composites was increasing. Figure 4.6 shows the variation in resistivity of pure nitrile rubber vulcanizates with the concentration of acetylene black at room temperature. At low concentration of acetylene black, the resistivity of the sample was very high. This was because, the particles of acetylene black were isolated from each other and a conducting through-going path was not formed. As the amount of acetylene black was increased, the resistivity decreased rapidly up to 40 phr of acetylene black and there after, the decrease in resistivity was very slow. It was due to the formation of aggregates of acetylene black particles to form a conducting path through the polymer chain. Once saturation was reached, contact resistance between the clusters was no longer significant and so at higher loadings, the decrease in resistivity was not rapid.

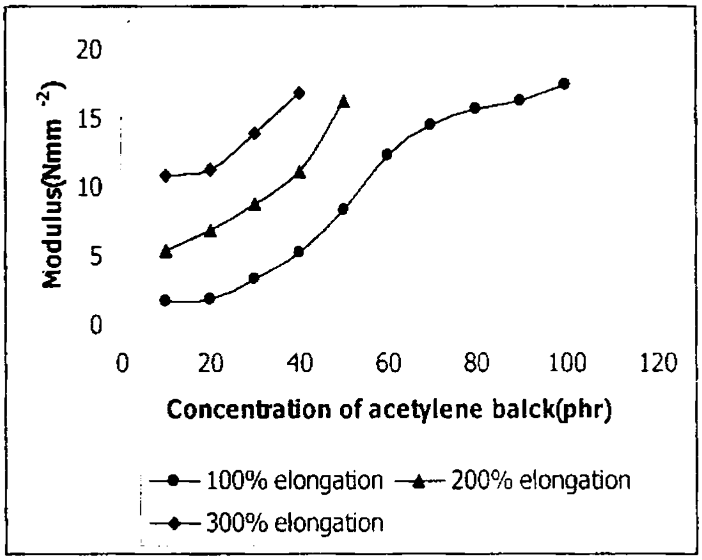

Fig. 4.5 Variation in modulus of vulcanizates with the amount of acetylene black

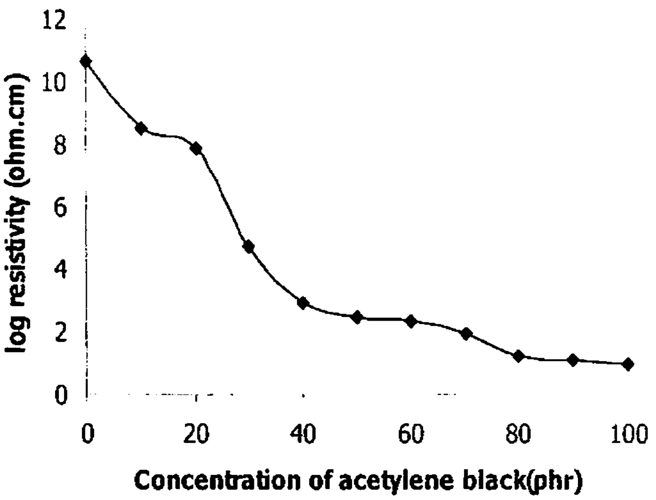

Fig. 4.6 Variation in resistivityof vulcanizates with the amount of acetylene black

4.4 PART II

Studies On Conductivity of Blends of NBR With NR, EPDM And PVC

4.4.1 Sample preparation

NBR/NR and NBR/EPDM blends were prepared by masticating the individual rubbers separately and then mixing well on the two-roll mill and the other ingredients were added according to the formulation given in the Table 4.2.

NBR/PVC blend was prepared on a Brabender Plasticorder PL3S at a rotor speed of 40 rpm at 150^0 C as per the formulation given in Table 4.3. PVC was

Table 4. 2 Formulation of compounds (phr)

Mix	B_1	B_2	B_3
NBR	80	80	80
NR	20	-	-
EPDM	-	20	-
PVC	-	-	20
AB	60	60	60
ZnO	4	4	4
SA	2	2	2
S	1.5	1.5	1.5
MBTS	1	1	1
TMTD	0.5	0.5	0.5
DOP	6	6	6

Table 4.3 Formulation of PVC Mix

Materials	Amount (phr)
PVC	20
DOP	6
MgO	0.6
ZnO	0.6
SA	0.4

mixed with DOP and stabilizer , melted in the Plasticorder ,then NBR was added and mixing was continued for 5 more minutes. Other ingredients were added to this NBR/PVC mix on a two-roll mill as per the formulation given in Table 4. 2.

4.4.2 Results and discussion

The cure time and the mechanical properties of different blends of NBR with NR, EPDM and PVC are given in Table 4.4. NBR/PVC blend was having more hardness than NBR/NR and NBR/EPDM blends. It was due to the presence of PVC in the vulcanizate, which is a thermoplastic material. At the same dosage of acetylene black, the NBR/PVC vulcanizate had higher tensile strength and modulus compared to NBR/NR and NBR/EPDM blend. The tensile strength and modulus of the blend depends on the individual polymers and their compatibility.

Table 4.4 Properties of the Mixes

80/20 Blend	Cure Time at 150^0C (in min.)	Hardness (Shore A)	Elongation at Break (%)	Tensile Strength (N mm^{-2})	Modulus at 100 % elongation (N mm^{-2})
NBR/NR	4.16	83	189.58	15.69	9.97
NBR/EPDM	3.64	80	221.42	9.62	9.37
NBR/PVC	4.6	90	186.86	17.26	13.59

The variation in electrical resistivity on adding acetylene black to different blends of nitrile rubber with PVC, NR and EPDM is shown in Figure 4.7. NBR/NR blend had low resistivity than NBR/EPDM blend whose resistivity was lower than NBR/PVC blend. This behavior can be explained by the difference in the dispersion of acetylene black in different phases as well as in the interphase. Blends always have more conductivity compared to the individual polymer. This was due to the selective localization of acetylene black in one phase or at the interphase of the polymer matrix[12].

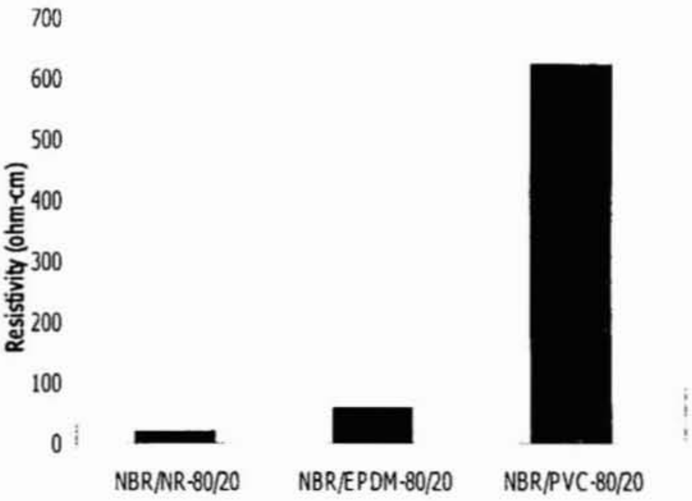

Fig. 4.7 Variation in resistivity of vulcanizates with the amount of acetylene black

With some exceptions, compatibility of the components of a blend may roughly be predicted by the solubility parameters of the components. The nearer the values of solubility parameters, the better will be the compatibility. Table 4.5 shows the solubility parameters of the polymers used[9].

Table- 4.5 Solubility parameter of the polymers

Polymer	Solubility parameter $(J/m^3)^{1/2} \times 10^{-3}$
EPDM	16
NR	16.2
PVC	19.8
NBR	20.5

NR and NBR differ widely in polarity. NBR is a polar rubber, while NR is a nonpolar rubber. They have quite different solubility parameters as given in Table-4.5 and this results in limited degree of mixing at the interphase of the blend. So when their blends were prepared, the acetylene black got dispersed at the interphase between the two rubbers. So the number of contact points was increased and the gap width between the aggregates of acetylene black particles were decreased. So a conducting path was easily formed and the conductivity was increased. The conductivity of NBR/NR blend was more than that of pure NBR and NR vulcanizates.

NBR/PVC blend is technically compatible at all ratios. Their solubility parameters are very close to each other. NBR acts as a nonmigrating plasticizer to PVC[13]. Presence of a plasticizer decreases the conductivity. It can be explained by the well dispersion of acetylene black in NBR/PVC blend. There was no localization of acetylene black aggregates, by which, the number of contact points were decreased and the gap width was increased. Therefore the conductivity was lower than pure NBR vulcanizates as well as NBR/NR and NBR/EPDM blends.

It is evident from Table- 4.5 that the NBR/EPDM blend, which has a large difference in solubility parameter, should form an incompatible blend, and indeed it does. EPDM is generally placed between unsaturated, high diene rubbers (NR, SBR, BR, CR, NBR) and IIR (weak interaction), with regard to its interaction with black. Therefore, even though the NBR/EPDM blend is more incompatible than NBR/NR blend, the conductivity of NBR/EPDM blend was lower than that of NBR/NR blend. The exceptional behavior of NBR/EPDM blend is already reported[9].

4.5 PART-III

Studies On Conductive NBR/NR Blends

4.5.1 Sample preparation

NBR/NR blends of varying composition were prepared as per the formulation given in Table 4.6. 80/20 NBR/NR blends containing different amounts of acetylene black were prepared and the electrical conductivity and mechanical properties of the vulcanizates were studied.

Table 4.6 Formulation of compounds

Mix	C_1	C_2	C_3	C_4	C_5	D_1	D_2	D_3	D_4
NBR	80	70	50	30	20	80	80	80	80
NR	20	30	50	70	80	20	20	20	20
AB	60	60	60	60	60	60	70	80	90
ZnO	4	4	4	4	4	4	4	4	4
SA	2	2	2	2	2	2	2	2	2
S	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
MBTS	1	1	1	1	1	1	1	1	1
TMTD	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
DOP	6	6	6	6	6	6	7	8	9

4.5.2 Results and discussion

Figure 4.8 represents the variation in cure time of NBR/NR blends of varying composition, at the same dosage of acetylene black (60 phr). Cure time of the compounds was decreased with increase in the amount of NR in the blend.

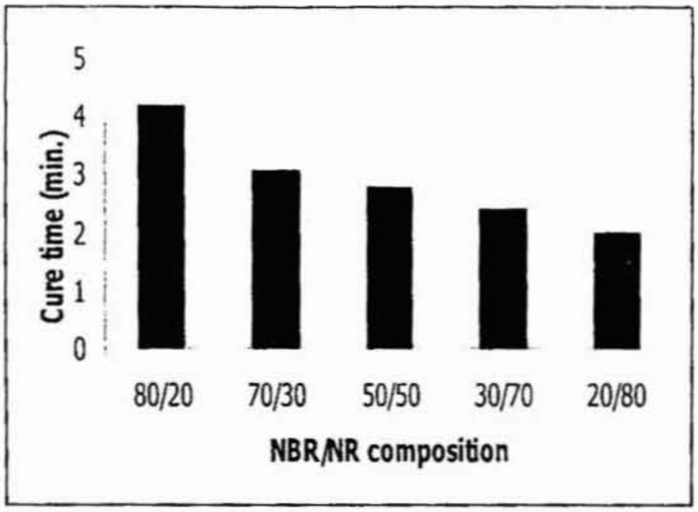

Fig. 4.8 Variation in cure time of vulcanizates with the composition of NBR/NR blends containing 60 phr of acetylene black

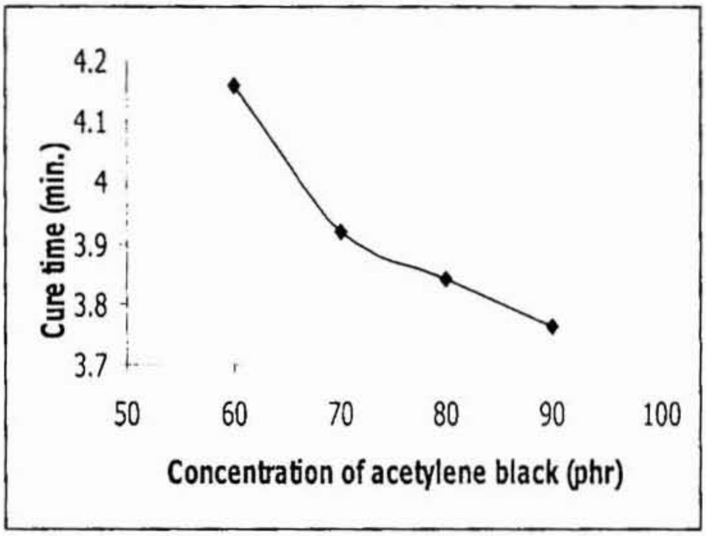

Fig. 4.9 Variation in cure time of vulcanizates of 80/20 NBR/NR blends with the concentration of acetylene black

This was because, the dispersion of sulphur was easier when the amount of NR was increased, and therefore fast curing takes place. Figure 4.9 shows the variation in cure time of 80/20 NBR/NR blends with the concentration of acetylene black. Cure time of the blends decreased with increase in the amount of acetylene black due to the accelerating effect of acetylene black on vulcanization. Table 4.7 gives the hardness, tensile strength and elongation at break of various blends.

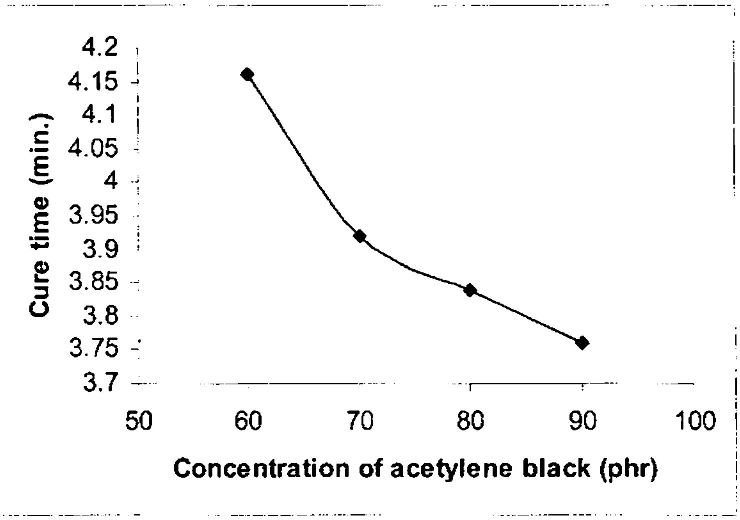

Fig.4.9 Variation in cure time of 80/20 NBR/NR blends with the concentration of acetylene black.

Figure 4.10 represents the variation in resistivity of NBR/NR blends of varying composition, at the same dosage of acetylene black (60 phr). The 80/20 - NBR/NR blends had the lowest resistivity compared to other blends. The graph shows there was a decrease in resistivity, and it reached a minimum value near 80/20-blend. This can be explained by the fact that, when the amount of one phase was small and the other phase was large, the acetylene black will be dispersed nonuniformly in the continuous phase and so the number of contact points were increased and the gap width was decreased. When both the polymer become approximately equal, the acetylene black will be uniformly dispersed in both phases and the continuity of the conducting path will be decreased, which resulted in a decrease in conductivity. Depending on the interaction of polymer with the acetylene black, there may be redistribution of acetylene black from the component with less interaction with the elastomer zone with more black-rubber interaction (at the interface of two elastomers) [9,10]. The distribution of acetylene black also depends on the solubility parameter of the individual elastomers of the blends.

Table 4. 7 Properties of the Mixes

Mix No.	Hardness (Shore A)	Elongation at Break(%)	Tensile Strength (N mm^{-2})
C_1	83	189.58	15.69
C_2	90	182.81	14.66
C_3	85	176.88	14.86
C_4	90	154.3	13.8
C_5	80	221.3	17.46
D_1	83	189.58	15.69
D_2	90	132.86	16.7
D_3	90	160.45	17.99
D_4	91	143.51	18.77

Figure 4.11 shows the variation in resistivity of 80/20-NBR/NR blends with the concentration of acetylene black. Resistivity was decreased with increase of acetylene black concentration. i.e., the electrical conductivity of the vulcanizates increased with increase in the amount of acetylene black similar to NBR vulcanizates.

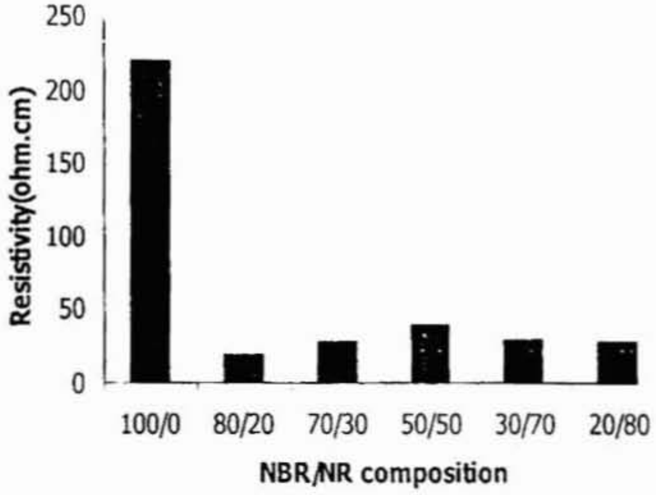

Fig. 4.10 Variation in resistivity of vulcanizates with the composition of NBR/NR blends containing 60 phr of acetylene black

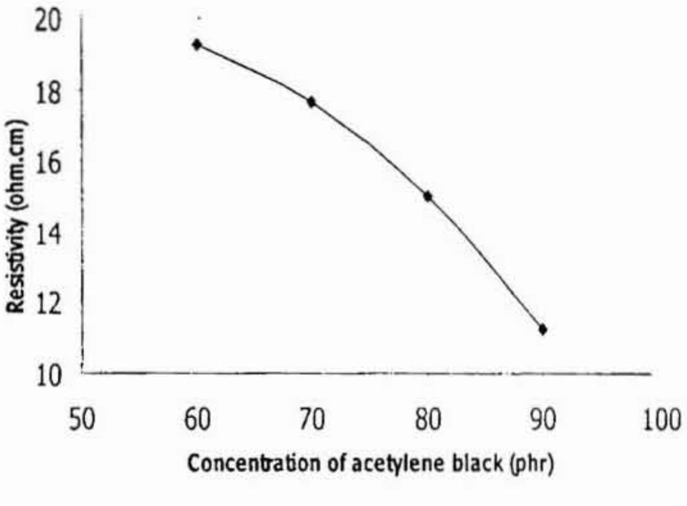

Fig. 4.11 Variation in resistivityof 80/20 NBR/NR blends with the concentration of acetylene black

4.6 PART- IV

Effect Of Temperature On The Electrical Conductivity Of NBR And Its Blends With NR, EPDM And PVC

4.6.1 Results and Discussion

Figures 4.12- 4.19 represents the variation in resistivity of different vulcanizates with temperature. When temperature was increased from 25^{0}C to 150^{0}C, the resistivity of all compounds increased at first, and then decreased. Similarly, on cooling, the resistivity of all compounds at first decreased, and then at low temperature, the resistivity further increased with temperature. For different vulcanizates, the temperature at which the change in resistivity takes place was different and it depends on the composition of the different vulcanizates. All compounds which contain acetylene black has a chain of aggregates of acetylene black as well as there are insulating interlayers of the polymer.

As the temperature was increased, the resistivity at first increased and at higher temperature region, the resistivity of the vulcanizates slightly decreased. This unexpected behaviour in NBR vulcanizates was attributed to the simultaneous occurrence of two competing processes. First, there was an increase in resistivity, due to the thermal expansion of nitrile rubber, which was higher than that of acetylene black, resulting in an increase in the gap width between the aggregates; and with increasing temperature, some of the aggregates of acetylene black breaks down and so the gap width between the aggregates increased and so conductivity was decreased. The second process comprises activation of conductivity at relatively high temperatures, as in non-crystalline semi-conductors [12]. The occurrence of the observed anomalies depends on the nature and the degree of filling of the carbon black used [14], on the mixing process, and on the extent of thermo-oxidative ageing[15].

On cooling, the resistivity of the vulcanizates at first decreased. This may be either due to the contraction of nitrile rubber so that the gap width between aggregates of acetylene black decreased or due to the reagglomeration of the particles resulting in a decrease in gap width[3,5,6]. At low temperature, the resistivity further increased or remained as constant. This was because, at low temperature, the reagglomeration of the acetylene black particles may be complete in NBR and also, the contraction of the rubber may not be changing the gap width between the aggregates.

The nature of the hysteresis loop in the $\rho = f(T)$ curve during the heating-cooling cycle is shown in figures 4.12- 4.19 . It has reported that the hysteresis loop results from the thermal mismatch between filler and polymer[6,16]. The uneven thermal expansion of nitrile rubber and acetylene black may be one of the reasons for the creation of a hysteresis loop.

Figure 4.12 shows the variation in the resistivity of nitrile rubber vulcanizate with 60 phr of acetylene black with temperature. When temperature was increased, some of the aggregates of carbon black break down and the gap width between the aggregates increased and so the resistivity was increased up to about 55^{0}C and thereafter the resistivity decreased with increase in temperature. The decrease in resistivity may be due to the thermal activation of charge carriers present in the rubber matrix[12]. A similar observation has been reported earlier by Abo-Hashem and colleagues[5] in butyl rubber mixed with SRF carbon black. They have observed a decrease in conductivity below 60^{0}C for the composites containing 40 and 70 phr SRF; above 60^{0}C, thermally activated behaviour show an increase in conductivity during the heating cycle. It was reported that the structure of SRF black suffers from slight breakage below 60^{0}C and reformation above 60^{0}C, wherein the increase in free volume holes becomes appreciable. Silicone rubber containing ISAF black (N-234) also has been reported[3] to show an unexpected observation like this. So the resistivity decrease may also be due to the reformation of acetylene black aggregates in the heating cycle itself.

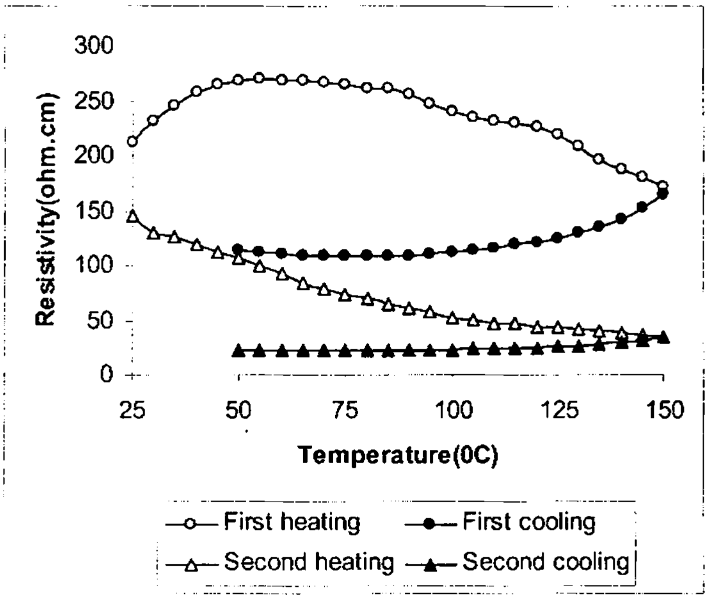

Fig. 4.12 Variation in resistivity with temperature for nitrile rubber vulcanizate with 60 phr acetylene black

On cooling, reagglomeration of the particles took place, the gap width between the aggregates of acetylene black decreased, and the conductivity increased. During cooling, the size of the aggregates of acetylene black may be greater than that at the heating time. This may be one of the reasons for the higher conductivity on cooling than on heating; thus the hysteresis loop resulted. Also, it has been reported [9] that the resistivity of silicone rubber compounds decreased after heat ageing at 150-250^{0}C. The decrease in resistivity during ageing was explained to be due to the increase in the concentration of the carbon black in the system, as a result of a loss of mass (3.8% after 55000 hrs at 150^0 C). Here also after heating cycle, aging of nitrile rubber takes place, and the conductivity on cooling was higher than on heating; thus, the hysteresis loop was formed.

The resistivity values shown in the graph during the cooling cycle was only up to 50^{0}C, because the cooling rate was very low below 50^{0}C. If we extrapolate the curve to room temperature, the cooling cycle endpoint will be the same as that of the starting point of the second heating cycle. The heating-cooling cycle was repeated for checking the reproducibility of the variation in conductivity with temperature. The resistivity was decreased on heating and remained constant on cooling during second cycle. This was because, some permanent change due to ageing takes place for the rubber and a steady state was reached after one cycle.

Figure 4.13 shows the variation in the resistivity of 80/20 NBR/PVC blend with temperature containing 60 phr of acetylene black On heating, resistivity of the vulcanizate was increased up to 40^{0}C and thereafter the resistivity decreased with increase of temperature. On cooling, the change in resistivity was very low compared to that in the heating cycle, and the resistivity slowly decreased with decrease in the temperature .In the second cycle, the variation in resistivity with temperature was very low. This may be because, a steady state might have reached after one heating –cooling cycle from 25- 150^0 C.

Figure 4.14 shows the temperature dependence of resistivity for 80/20 NBR/EPDM blend containing 60 phr of acetylene black. On heating, the resistivity increased up to 75^{0}C, due to the thermal expansion of the nitrile rubber. This may also be due to the disintegration of acetylene black aggregates. At higher temperature, the resistivity decreased with increase of temperature. On cooling, the resistivity decreased due to the contraction of nitrile rubber and may also be due to the reagglomeration of acetylene black particles. In the second cycle, the variation in resistivity with temperature was very low. This may be due to the steady state reached after one heating –cooling cycle from 25- 150^0 C as in NBR/PVC blend.

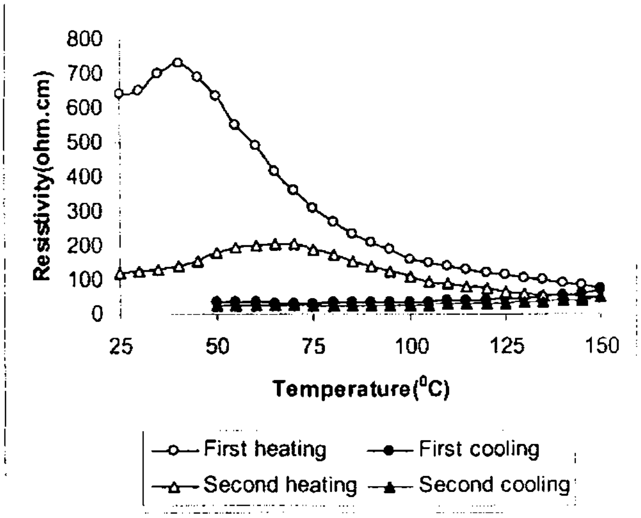

Fig. 4.13 Resistivity variation with temperature for 80/20 NBR/PVC blend containing 60 phr of acetylene black

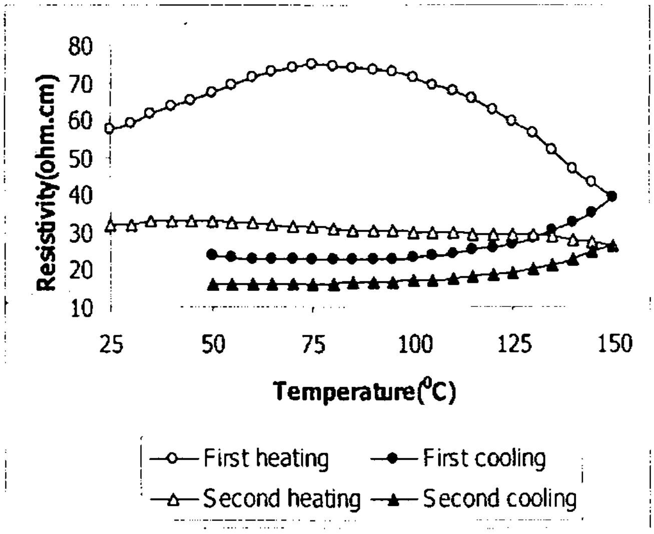

Fig. 4.14 Resistivity variation with temperature for 80/20 NBR/EPDM blend containing 60 phr of acetylene black

Figures 4.15- 4.19 shows the temperature dependence of resistivity for NBR/NR blends of different composition containing 60 phr of acetylene black. On heating, the resistivity was increased first, due to the thermal expansion of the nitrile rubber and disintegration of acetylene black aggregates. At higher temperature, the resistivity decreased with increase of temperature, due to the thermal activation of conductivity. On cooling, the resistivity decreased, and the change in resistivity was similar to that of pure NBR vulcanizate mixed with acetylene black. In the second cycle, the variation in resistivity with temperature was very low.

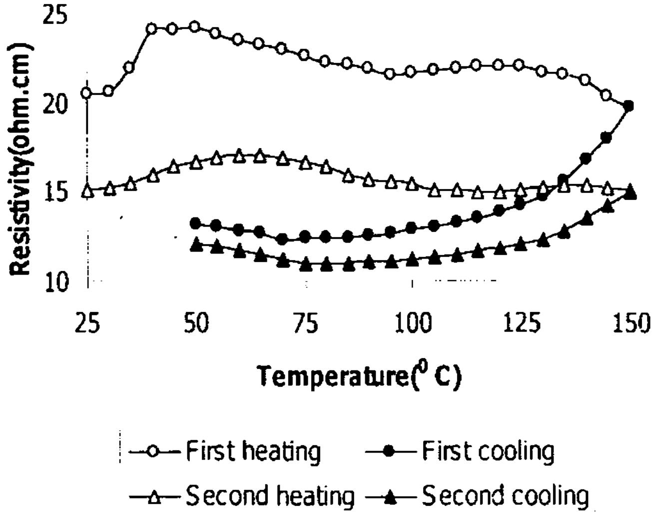

Fig. 4.15 Resistivity variation with temperature for 80/20 NBR/NR blend containing 60 phr of acetylene black

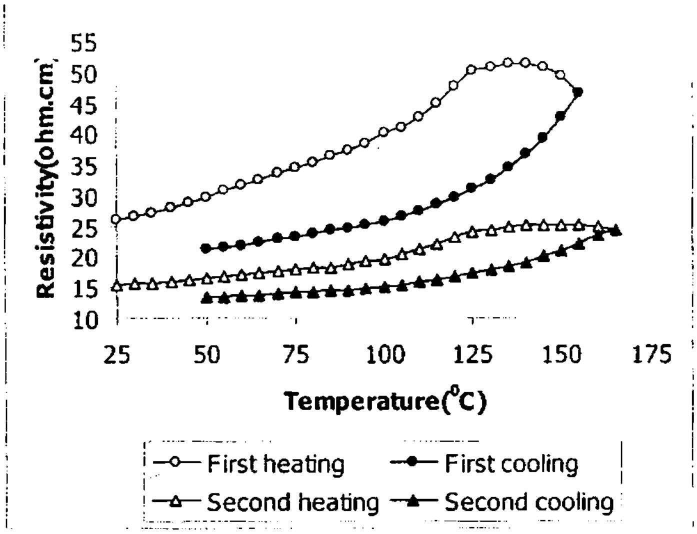

Fig. 4.16 Resistivity variation with temperature for 70/30 NBR/NR blend containing 60 phr of acetylene black

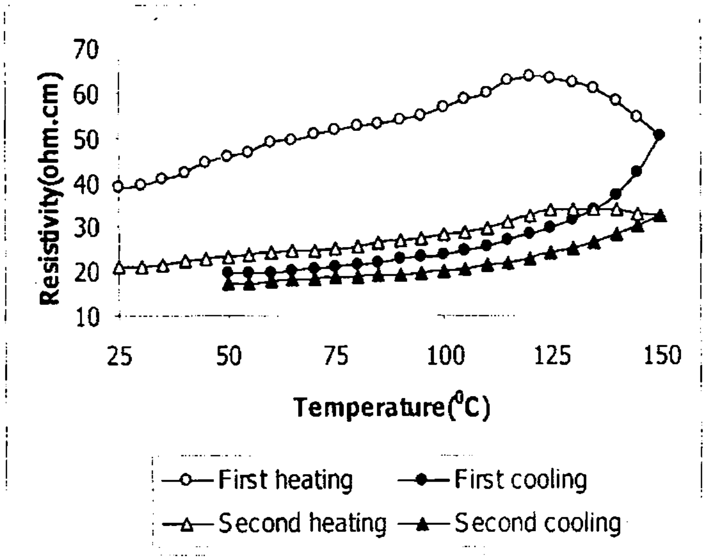

Fig. 4.17 Resistivity variation with temperature for 50/50 NBR/NR blend containing 60 phr of acetylene black

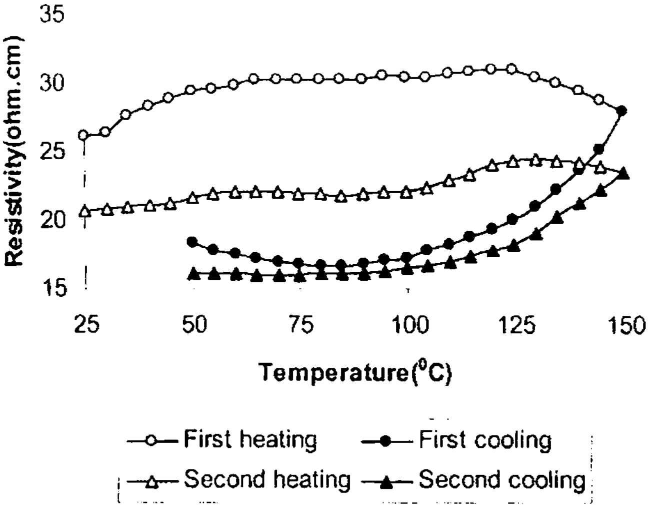

Fig. 4.18 Resistivity variation with temperature for 30/70 NBR/NR blend containing 60 phr of acetylene black

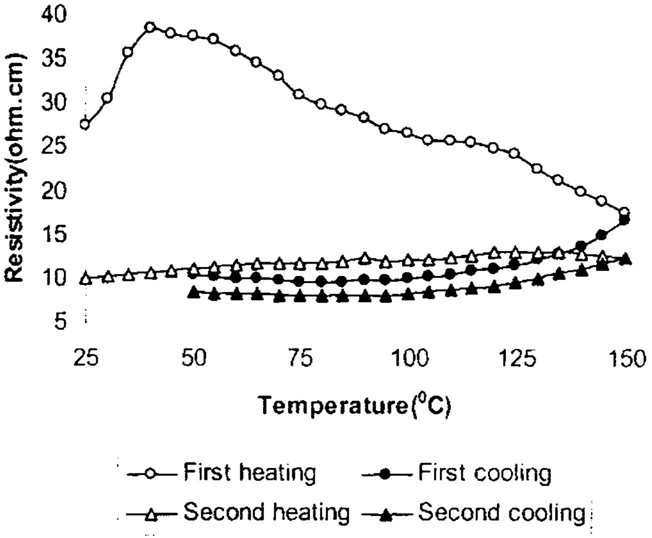

Fig. 4.19 Resistivity variation with temperature for 20/80 NBR/NR blend containing 60 phr of acetylene black

4.7 Conclusions

1 The electrical conductivity of nitrile rubber vulcanizates was increased with the amount of acetylene black.

2 Blends of nitrile rubber with NR, PVC and EPDM were more conducting than pure NBR vulcanizates, containing the same amount of acetylene black.

3 NBR/NR blends were more conducting than NBR/EPDM and NBR/PVC blend, at the same dosage of acetylene black.

4 80/20 - NBR/NR blend was more conducting than other NBR/NR blends, at the same dosage of acetylene black.

5 Electrical conductivity depends on the degree of dispersion of acetylene black at the interphase and the polymer matrix in the case of polymer blends.

6 The electrical conductivity of the NBR vulcanizates decreased with increase in temperature at first and thereafter the conductivity increased with increase in temperature during the heating cycle.

7 During the cooling cycle, the conductivity increased at first and then decreased slowly.

8 The change in conductivity during the cooling cycle was negligible compared to that during the heating cycle.

9 The change in conductivity during the second heating-cooling cycle was very low compared to that in the first cycle.

4.8 References

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Chapter 5

PREPARATION AND CHARACTERIZATION OF A NEW CONDUCTING POLYMER - POLY(P- PHENYLENEDIAZOMETHINE)

5.1 Introduction

Conducting polymers offer two potential advantages over the traditional inorganic materials used as conductors. First, processing of conducting polymers by moulding and other plastics processing techniques into various electrical and electronic devices and forms is easy compared to metallurgical processes used for inorganic conducting materials. Second, the lightweight property of polymeric materials would make certain types of applications more practical and economical. The biggest and most immediate potential application for conducting polymers is lightweight rechargeable batteries for portable tools and vehicles. Conducting polymers would serve both current carrying and ion- conducting functions by replacing traditional electrode and electrolyte substances[1].

The structural requirement for a conducting polymer is a conjugated π electron system. Extended conjugation in the polymer backbone is attained in two ways, either by the interaction of π electrons of the conjugated carbon-carbon double bonds or by the interaction of π electrons of carbon-carbon double bonds with nonbonding electrons of heteroatoms, such as S, N, P, etc. present in the polymer chain. They can be easily oxidised or reduced by charge –transfer agents, which are called dopants. Dopants are of two types: - 1) Oxidative dopants, which are electron attracting substances, eg; - AsF_5, I_2, $AlCl_3$, $FeCl_3$, $HClO_4$, SO_3 etc. and 2) reductive dopants, which are electron donating substances. eg:- sodium naphthalide , Na/K alloy, molten potassium, LiI etc. Electrons are removed from (p-doping) or added to (n-doping) the conjugated pi-electron system to form extra holes or electrons, respectively, which carry current through the polymer chain. In addition to oxidation or reduction, the dopants act as a bridge or connection for carrying current between different polymer chains.

Chemical reactivity of the dopant is of prime importance in obtaining a conducting polymer. Not all dopants are equally capable of oxidizing or reducing a polymer chain. For example, iodine is a dopant for increasing electrical conductivity of polyacetylene by 13 orders of magnitude but is too weak to oxidize polyphenylene sulphide or polyparaphenylene. AsF_5 is strong enough to oxidize these two polymers. Doping conditions also play an important role. Higher homogeneity in the sample results from slower rate of doping and that affects the electrical conductivity. Electrical conductivity usually increases with the doping level due to increase in the charge carrier concentration.

The characteristics of conducting polymers that are different from metals are summarised below.

1 Mass production is preferred in respect of costs.

2. These are of low density and therefore conducive to energy conservation.
3. They can be made into films very easily to provide materials which have a large surface area
4. They are very sensitive to external stimuli.
5. Electrically anisotropic materials can be obtained.
6. These materials are not so liable to the effects of oxidation.
7. These materials have the ability to absorb large quantities of liquids and gases.
8. They have good processabilities
9. Porous conductors can be made without difficulty.

In recent years, the synthesis of conducting polymers has attracted great interest due to their electrical, electrochemical and optical properties[2]. They have widespread applications in rechargeable batteries [3,4], electrochromic devices [5], gas separation membranes [6], and enzyme immobilization [7]. The conducting polymers such as polypyrrole, polythiophene, polyfuran and polyaniline have been examined for electronic and chemical applications[8,9]. Applications of polythiophene for electrooptical switching and memory devices[10], and organic batteries[11] have been proposed. Polypyrrole doped with sulphonate derivatives of metallo porphyrin is reported to be useful in the cathodic reduction of oxygen in acidic and basic solutions, which find applications in fuel cells and metal/air batteries[12]. It has been demonstrated that[13] the chloride-doped polypyrrole film shows a stable and selective response towards Cl^- ions in solution. It has been also reported that Pt electrode modified with polypyrrole can be used as a nitrate sensor[14].

Mac Diarmid et.al. have assembled a battery, making use of the amphoteric nature of polyacetylene, to provide a prototype of plastic battery[15]. Rechargeable batteries involving polyaniline, polypyrrole, or polyparaphenylene / alkali metal cathode also has been developed[16]. Narkis[17] has suggested that cross-linked polyethylene filled with carbon black is ideal as a material for preventing the build-up of static electricity. Polyphenylenevinylene and derivatives are used as light-emitting diodes, and lightly doped polyaniline film membranes are used for the separation of gases.

Poly (azomethine)s, sometimes called poly(schiff bases), are a group of polymers which are catching more attention due to the following reasons. Aromatic poly(azomethine)s are highly thermo-stable in analogy to aromatic polyethers. Further more, poly (azomethine)s may possess a conjugated main chain and, after suitable doping, may show an attractive level of electric conductivity [18].

Only a few poly (azomethine)s derived from aliphatic dialdehydes and aromatic diamines were described in literature, and most of them were prepared by solution condensation of diamines and glyoxal [19-21]. High yields and satisfactory elemental analyses were reported, but no information on viscosity and molecular weights.

In the present study, a new conducting polymer based on glyoxal and p-phenylene diamine was synthesized. The synthesis of poly(p-phenylenediazomethine) was carried out in different solvents, like, methanol, toluene, m-cresol and DMF. First the reaction was carried out in methanol. Since the conductivity of the product formed was very low, the polymerization was repeated in toluene solvent. In this medium also, the conductivity of the product formed was very low and the reaction was repeated in m-cresol. Even though the conductivity of the product was higher than other samples already prepared, the yield of the product was very low. So the polymerization was carried out in DMF as the solvent.

5.2 Experimental

5.2.1 Materials

P-phenylene diamine, Glyoxal 40 % solution, Glyoxal hydrate (trimer), N,N-Dimethyl formamide (DMF) , m-Cresol , Toluene , Methanol, Acetone , Hydrochloric acid (HCl), Perchloric acid ($HClO_4$), Iodine (I_2), and Carbon tetra chloride (CCl_4) was used in the present investigation conforming to the specifications given in Chapter 2.

5.2.2 Synthesis of poly(p-phenylenediazomethine) in methanol

0.1mole of p-phenylene diamine was dissolved in methanol (300ml) and 0.1mole glyoxal (40% solution) was added drop wise with continuous stirring for 2 hours. By that time, precipitation of the product takes place. The product was washed with water and then with methanol and dried well at room temperature under vacuum.

5.2.3 Synthesis of poly(p-phenylenediazomethine) in toluene

0.1mole of p-phenylene diamine was added to 400 ml of toluene and was dissolved by stirring. Then 0.1 mole of glyoxal was added to it and stirred well. The mixture was slowly heated to boiling, with continuous stirring, and was refluxed at the boiling temperature for 5 hours. By that time, the precipitation of the product takes place. It was then allowed to cool to room temperature and then poured into excess of ice-cold water. It was allowed to settle, filtered, washed with plenty of water until the filtrate was colorless. Then it was washed with methanol, and allowed to dry at room temperature in air for one day. Then the final drying of the sample was done at 70^0C under vacuum.

5.2.4 Synthesis of poly(p-phenylenediazomethine) in m-cresol

0.1mole of p-phenylene diamine was added to 100 ml of m-cresol and was dissolved by stirring. Then 0.1 mole of glyoxal was added to it and stirred well. The mixture was slowly heated to boiling, with continuous stirring, and was refluxed at the boiling temperature for 4 hours. It was then allowed to cool to room temperature and then poured into excess of ice-cold water. The precipitate was allowed to settle, filtered, washed with plenty of water until the filtrate was colourless. Then it was washed with methanol, and allowed to dry at room temperature in air for one day. Then the final drying of the sample was done at 70^0C under vacuum.

5.2.5 Synthesis of poly(p-phenylenediazomethine) in N,N-dimethylformamide

0.1mole of p-phenylene diamine was added to 300 ml of DMFand was dissolved by stirring. Then 0.1 mole of glyoxal was added to it and stirred well. The mixture was slowly heated to boiling, with continuous stirring, and was refluxed at the boiling temperature for 4 hours. By that time, the precipitation of the product takes place. It was then allowed to cool to room temperature and then poured into excess of ice-cold water. It was allowed to settle, filtered, washed with plenty of water until the filtrate was colourless. Then it was washed with methanol, and allowed to dry at room temperature in air for one day. Then the final drying of the sample was done at 70^0C under vacuum.

The dried samples were powdered well, and, pelletized for the density and conductivity measurements. For the spectral and thermal studies, the sample was extracted with acetone until the extract was colorless, and dried well.

5.2.6 Doping

1g of each sample was put in 50ml each of 1M HCl solution, 1M $HClO_4$ solution and saturated solution of I_2 in CCl_4 and kept for 24 hours. Then it was filtered, washed with a little amount of acetone and dried at 70^0 C under dynamic vaccum for one hour.

5.3 Polymer Characterization

The prepared polymer samples were characterized by IR spectra, UV spectra, TGA, and Molecular weight determination (GPC), as explained in Chapter 2.

5.4 Measurements

5.4.1 D.C. conductivity

D.C. conductivity of the pressed pellets was determined by the two-probe technique. The samples were sandwiched between two copper electrodes and a constant voltage (6V) was applied to the sample. The current flowing through the sample was measured using a digital multimeter (APLAB model 1087). The conductivity of the sample was calculated using the equation, $\sigma = t / RA$, where 't' is the thickness of the pellet, 'R' is the resistance of the sample ($R = E / I$, where 'E' is the applied voltage and 'I' is the resulting current through the sample), and 'A' is the area of cross section of the pellet($A = \pi r^2$, where 'r' is the diameter of the pellet).

5.4.2 Density

Density of the pressed pellets were determined using the equation,

$D = M/V$, where 'M' is the mass of the pellet and 'V' is the volume of the pellet .

5.4.3 Microwave conductivity and Complex permittivity

The dielectric properties and conductivity of the samples were measured using cavity perturbation technique[22]. The experimental set up consists of a HP8510 vector network analyzer; sweep oscillator, S-parameter test set and rectangular cavity resonator. The measurements were done at 2.17 GHz at room temperature (25^0C).

In microwave studies the conductivity can be calculated using the equation,

Conductivity ,$\sigma = 2\pi f_s \varepsilon_0 \varepsilon_r''$

where 'f_s' is the resonant frequency, ε_0 is the complex permittivity of free space and ε_r'' is the imaginary part of the complex permittivity , which is given by the equation,

$\varepsilon_r'' = (V_c /4V_s)(Q_t' - Q_s / Q_t Q_s)$

where,' V_c ' is the volume of cavity, V_s is the volume of sample, Q_s is the quality factor of the cavity loaded with the sample and Q_t is the quality factor of the cavity with the empty sample holder.

The real part of the complex permittivity ε_r' is usually known as dielectric constant of the material. It can be calculated from the equation,

$\varepsilon_r' = 1 + (f_t - f_s)/ 2f_s (V_c /V_s)$

where f_t =resonant frequency of the unloaded cavity and f_s is the resonant frequency of the cavity loaded with the sample.

The pelletized samples were inserted into the cavity and the perturbation produced at a particular microwave frequency was noted. The resonant frequency and quality factor were recorded and dielectric constant and microwave conductivity were calculated using the above equations.

5.4.4 Thermal diffusivity

Thermal diffusivity was determined by photo acoustic technique. It can be defined by the mathematical expression, $\alpha = \kappa / \rho\ c_p$, where '$\kappa$' is the thermal conductivity, 'ρ' is the density and 'c_p' is the specific capacity at constant pressure.

5.5 Results and discussion

5.5.1 IR spectra

IR spectra of the polymer prepared in different solvents are given in the figures 5.1- 5.4. Figure 5.1 shows the IR spectrum of the sample prepared in methanol. The absorption band at 1678 cm^{-1} should be assigned to carbonyl absorption, possibly carbonyl of an amide group. The absorption band at 3306 cm^{-1} should be ascribed to a N-H stretching vibration. In literature the absorption of the –C=N- group is found between 1675 and 1660 cm^{-1}. However, if it is conjugated to an aromatic ring it shifts to a lower wave number, between 1635 and 1625 cm^{-1}. The absorption bands at 1517 and 1609 cm^{-1} shows the presence of an aromatic ring .The absorption band at 833 cm^{-1} can be assigned to the C-H out of plane vibration of the aromatic ring. Figure 5.2 shows the IR spectra of the sample prepared in toluene. This spectrum shows various spectral bands, which also occurs in the spectrum of p-phenylene diamine such as the bands at 3328, 3221,1855, 1639, and 1130cm^{-1}. From the spectrum, it may be concluded that the reaction was not completed in toluene solvent, hence the molecular weight of the product was very low, and hence the conductivity also was very low. The absorption band at 1662cm^{-1} should be assigned to carbonyl absorption, possibly a carbonyl of an amide group or to the –C=N- group. Fig.5.3 shows the IR spectra of the sample prepared in DMF. The absorption band at 1625 cm^{-1} may be assigned to a C=N stretching vibration. The absorption band at 1670 cm^{-1} should be assigned to carbonyl absorption, possibly a carbonyl of an amide group.

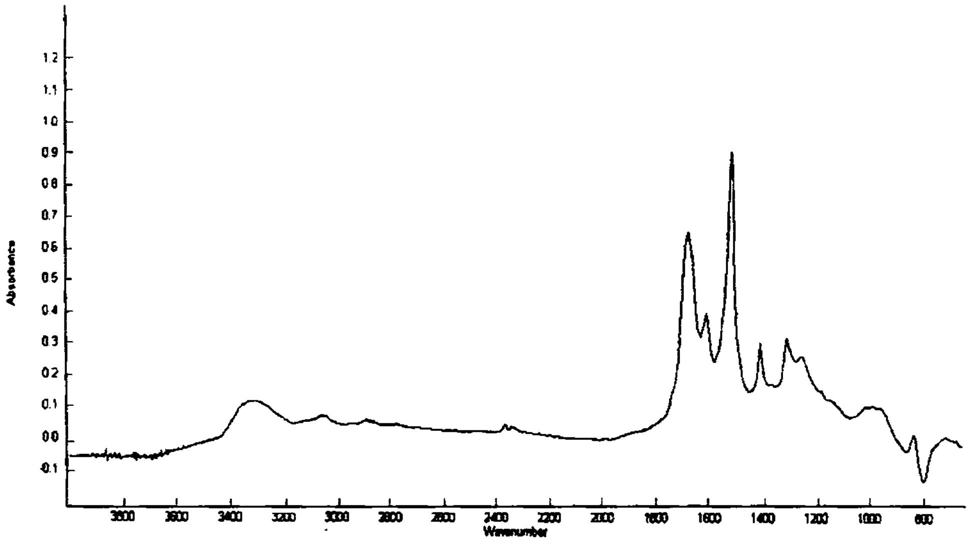

Fig. 5.1 IR spectrum of the sample prepared in methanol

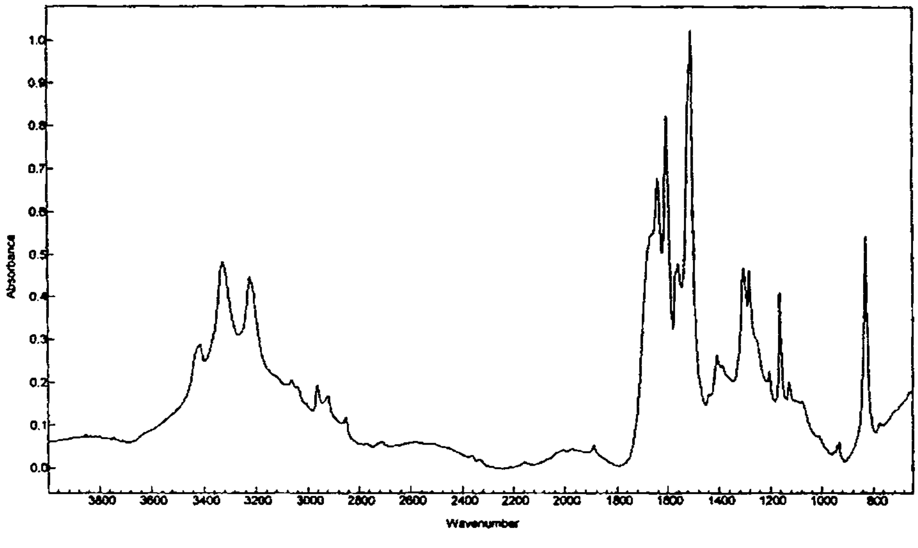

Fig.5.2 IR spectrum of the sample prepared in Toluene

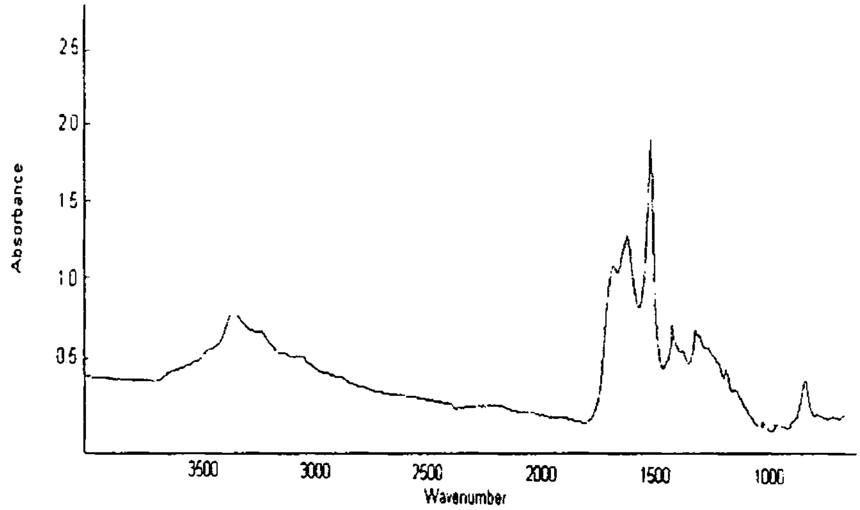

Fig.5.3 IR spectra of the sample prepared in DMF

The absorption band at 3350 cm^{-1} should be ascribed to a N-H stretching vibration. The absorption bands at 1512 and 1609 cm^{-1} shows the presence of aromatic ring.The absorption band at 833 cm^{-1} can be assigned to the C-H out of plane stretching vibration of aromatic ring.

Fig.5. 4 shows the IR spectrum of the sample prepared in m-cresol. This spectrum was comparable with that of sample prepared in DMF. Figure 5.5 compares the spectrum of the samples prepared in m-cresol and DMF. The main difference was the position and the intensity of the carbonyl band. In this sample, the center of this absorption was at 1699 cm^{-1}, while it was positioned at 1670cm^{-1} in sample prepared in DMF. Again there was an absorption band at 3350 cm^{-1} that can be assigned to an N-H stretching mode. Because of hydrogen bonding this absorption band was shifted to a lower wave number.

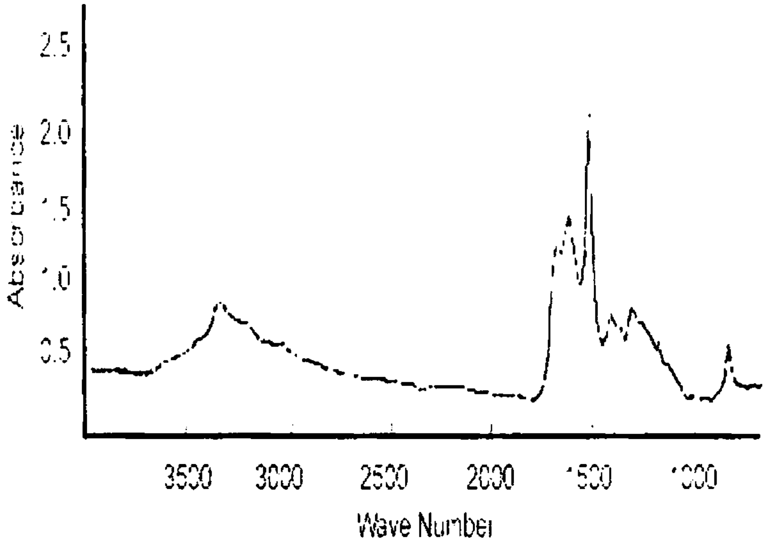

Fig.5. 4 IR spectrum of the sample prepared in m-cresol

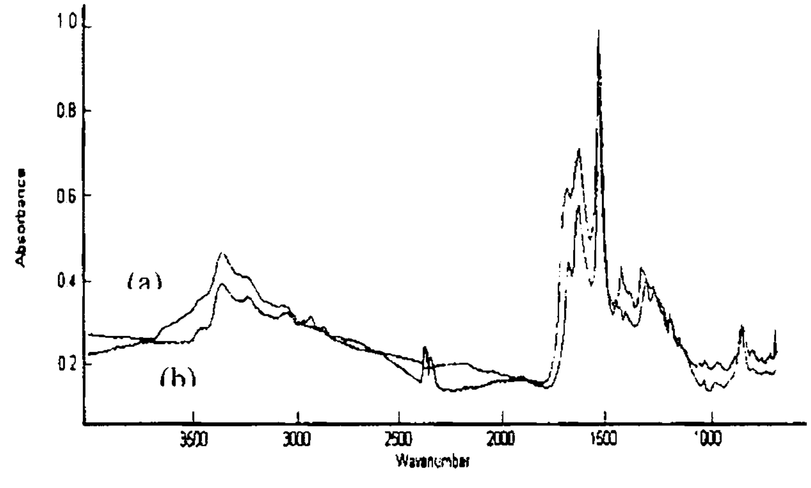

Fig.5.5 IR Spectra of the polymer prepared in (a) DMF and (b) m-cresol

Figure 5.6 compares the IR spectrum of the polymer prepared in toluene as the solvent and the monomer glyoxal. From the spectrum, it was clear that unreacted glyoxal was not present in the polymer prepared in toluene., since no peaks due to unreacted glyoxal was present in the spectrum.

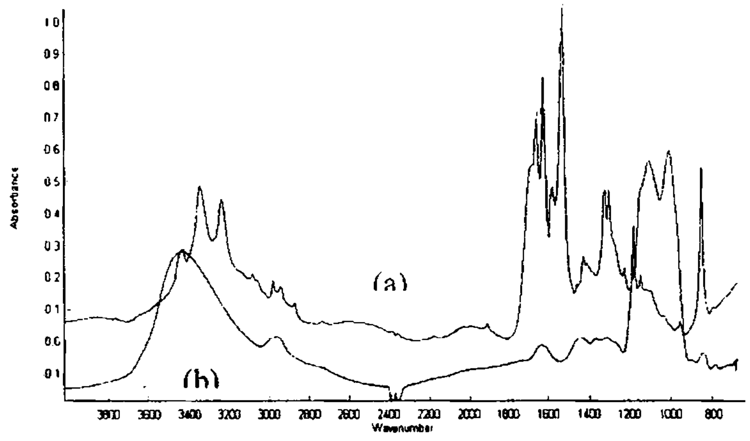

Fig.5.6 IR spectra of (a) polymer prepared in toluene and (b) the monomer - glyoxal

Figure 5.7 shows the comparison of the polymer prepared in toluene and the monomer paraphenylene diamine. This spectrum shows various spectral bands, which was also present in the spectrum of p-phenylene diamine such as the bands at 3328, 3221,1855, 1639, and 1130cm^{-1}. From the spectrum, it may be concluded that the reaction was not completed in toluene solvent and some amount of unreacted paraphenylene diamine was present in the polymer sample.

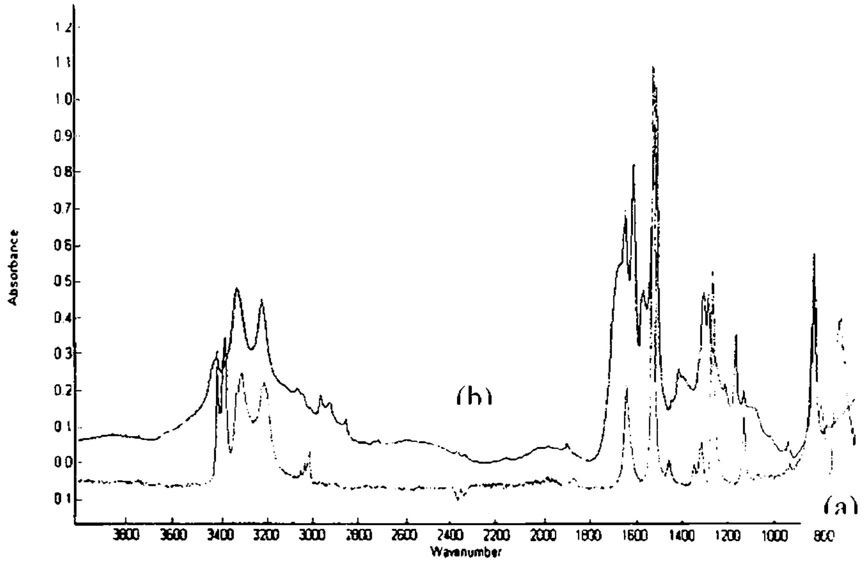

Fig. 5.7 IR spectra of (a) polymer - prepared in toluene and (b) monomer - paraphenylene diamine

Figure 5.8 shows the comparison of the spectrum of the polymer prepared in toluene and DMF. The two spectra were different from each other. The absorption band at 1639 cm^{-1} disappeared and a new band at 1625 cm^{-1} was present, which can be assigned to the –C=N- stretching vibration. The absorption band at 1670 cm^{-1} was present in both samples. Various spectral bands due to the presence of unreacted monomers disappeared in the spectrum of the polymer prepared in DMF.

Fig.5.9 shows the comparison of the spectrum of the polymer prepared in DMF and the monomers, glyoxal and p-phenylene diamine. From the figure, it was evident that, chemical reaction took place almost completely in the medium of DMF, since there was no spectral bands in the polymer sample due to the unreacted monomers, glyoxal and paraphenylene diamine.

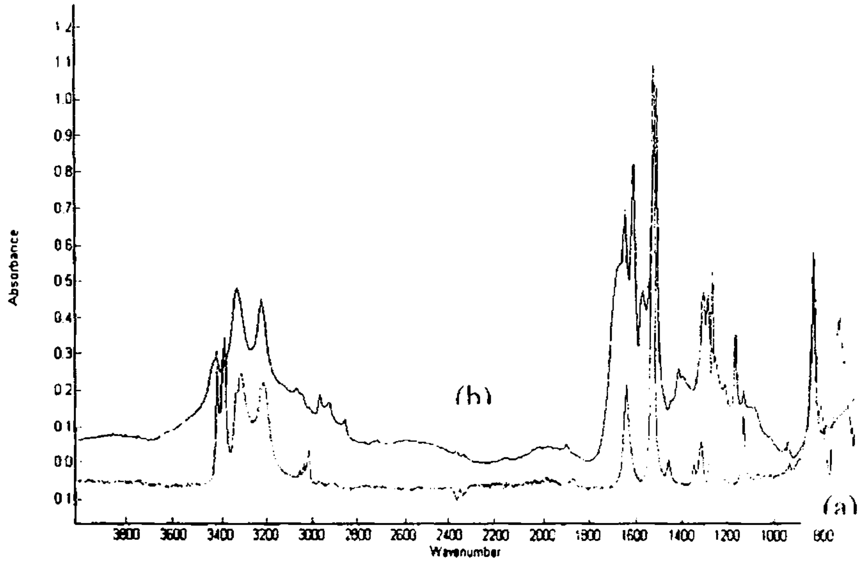

Fig. 5.7 IR spectra of (a) polymer - prepared in toluene and (b) monomer - paraphenylene diamine

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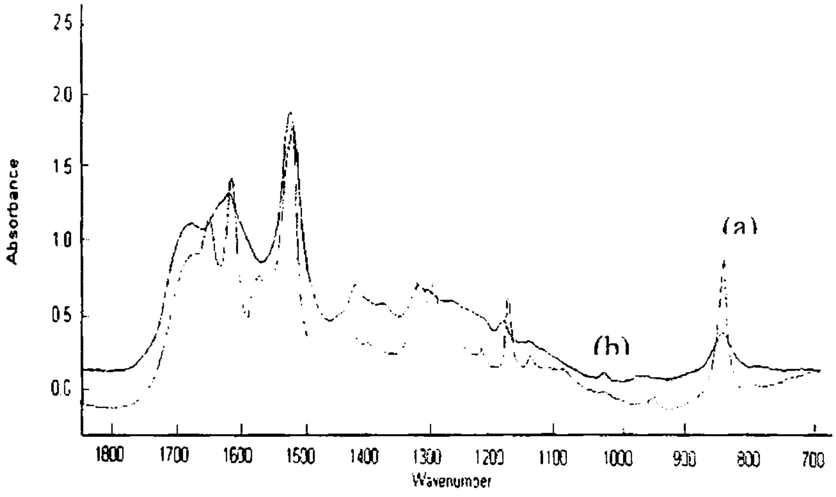


Fig.5.8 IR spectra of the polymer prepared in (a) toluene and (b) DMF.

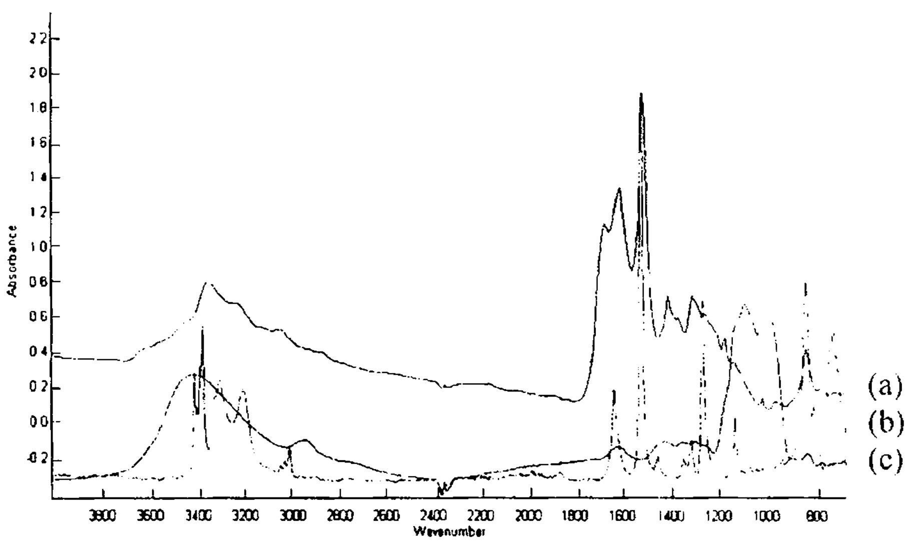


Fig.5.9 IR spectra of (a) polymer - prepared in DMF and the monomers (b) p-phenylene diamine and (c) glyoxal

Figure 5.10 gives the IR spectrum of the sample prepared in DMF, which was treated with triethyl amine. It was clear from the spectrum that there was no chemical change during this treatment. It was clear from the IR spectrum. Figure 5.11 compares the spectrum of the samples treated with triethyl amine and the original sample. The IR spectra of the samples do not differ from each other.

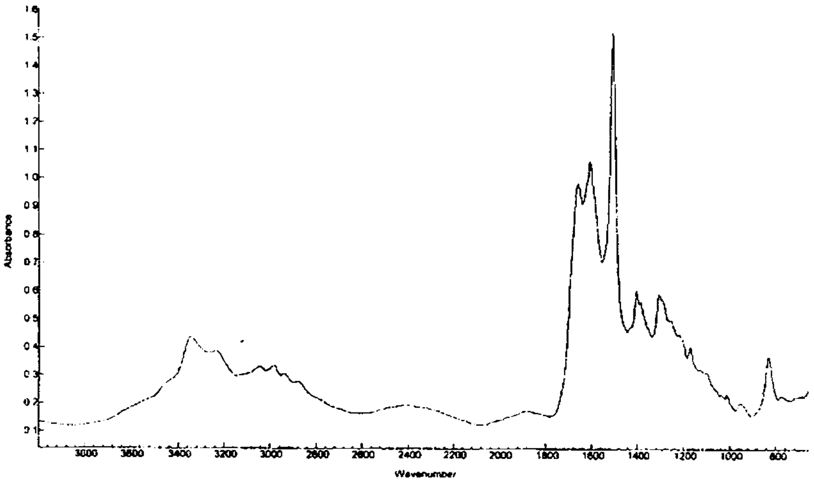


Fig.5.10 IR spectrum of the polymer prepared in DMF treated with triethyl amine

Effect of doping on the structure of the polymer was clear from the IR spectrum of the polymer prepared in DMF. Figure 5.12 shows the IR spectrum of the polymer doped with HCl. The additional peaks at 1016, 1124, and 1203 cm^{-1} can be assigned to be present due to the charge delocalization on the polymer backbone[23]. Broad peak in the region of 2500 - 2800 cm^{-1} was due to protonation on the polymer chain. Other peaks present in the spectrum were same as that present in the undoped polymer as given in figure 5.3.

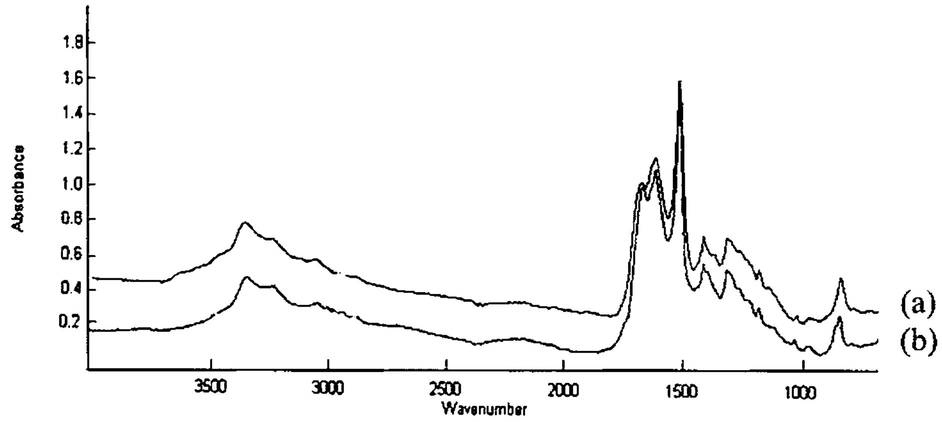


Fig.5.11 IR spectra of (a) polymer prepared in DMF (b) polymer treated with triethyl amine

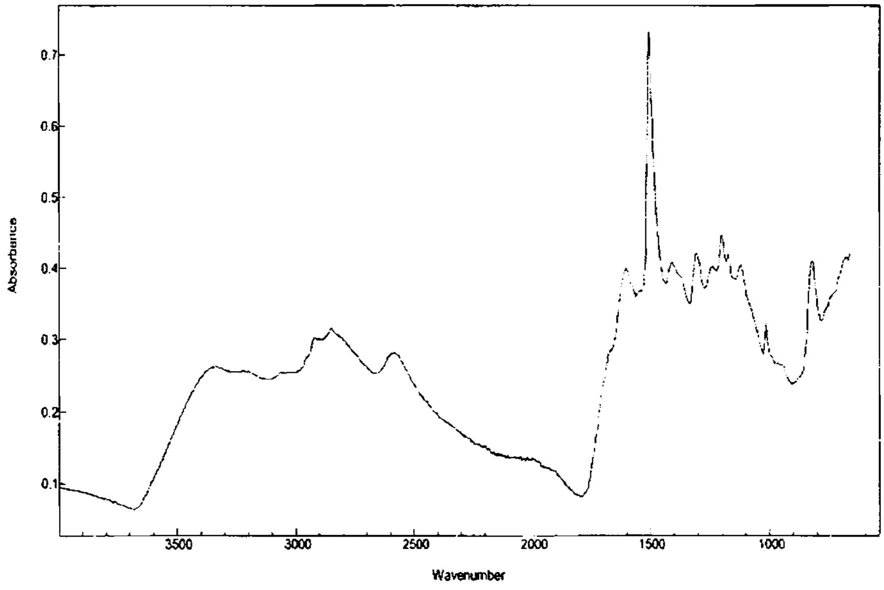


Fig.5.12 IR spectrum of the polymer doped with HCL

Figure 5.13 shows the IR spectrum of the polymer doped with $HClO_4$. The additional peaks at 1056 cm^{-1} can be assigned to be present due to the charge delocalization on the polymer bachbone. Broad peak in the region of 3200 cm^{-1} was due to protonation on the polymer chain. The peak at 3300 cm^{-1} of the undoped polymer had been shifted to 3500 cm^{-1}. Other peaks present in the spectrum were same as that present in the undoped polymer as given in figure 5.3.

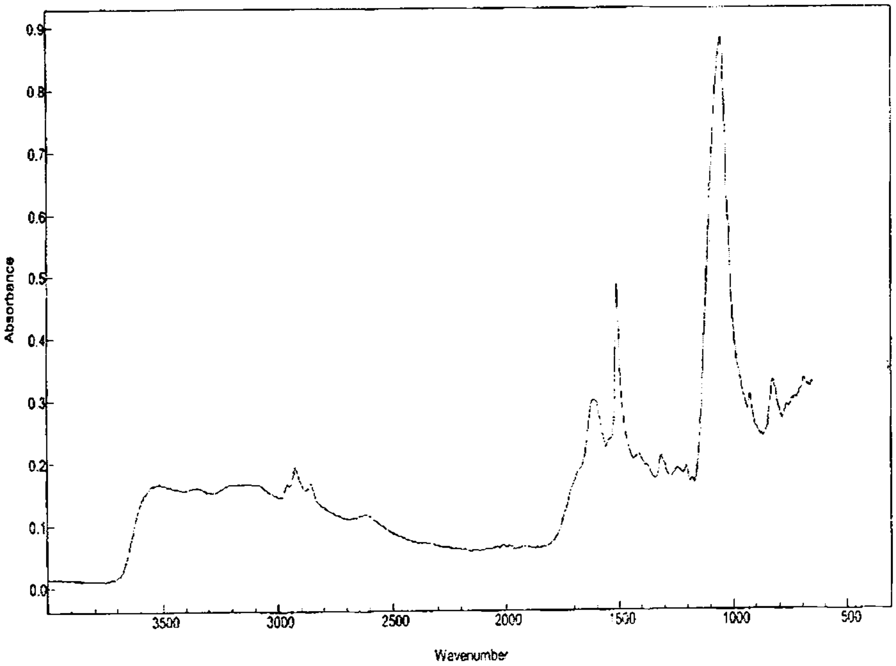


Fig.5.13 IR spectrum of the polymer doped with $HClO_4$

On comparing the two spectra, from the intensity of the additional peaks due to the dopant molecules, we can say that $HClO_4$ is a more stable dopant than HCl. The absorption bands at 1408 cm^{-1} and 1511 cm^{-1}due to the quinoid and benzenoid rings attached to N atom in the undoped polymer are shifted to 1410 and 1505 cm^{-1} ; and 1413 and 1508 cm^{-1} respectively for HCl and $HClO_4$ doped samples.

5.5.2 UV Spectra

UV absorption spectra of the polymer prepared in different solvents are shown in the figure 5.14. On changing the solvent from methanol to DMF, the wavelength at which maximum absorption occurs shifts to longer wavelength region. This shift is due to the extension of conjugation. All spectra show absorption in the region of 190-290nm. The absorption bands in this region is attributed to the n - π^* transition of the C=N chromophore[24]. λ_{max} of the polymer prepared in DMF is higher than that of other samples. This observation shows that the polymer has more conjugated double bonds when the synthesis was carried out in DMF as the solvent and minimum conjugation in the polymer prepared in toluene. This observation can also be related to molecular weight and conductivity of the polymer prepared in different solvents. D. C. conductivity of the polymer prepared in DMF is higher than that of other samples.

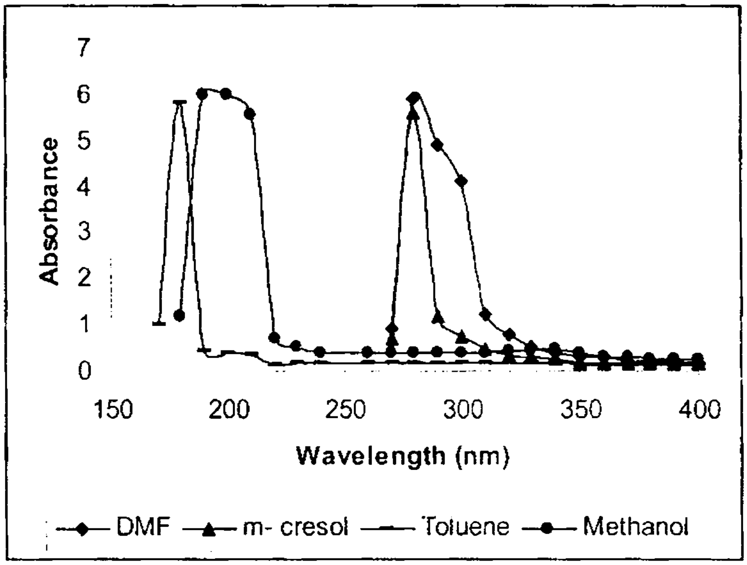


Fig. 5.14 UV spectra of poly(p-phenylenediazomethine) prepared in different solvents

5.5.3 GPC

The molecular weight of the polymer prepared in m-cresol as the solvent was determined using Hexafluroiso propanol as the eluent. Gel permeation chromatogram is shown in the figure 5.15. GPC distribution plot is given in Figure 5.16 and the results are given in Table 5.1. The number average molecular weight of the polymer was 25660 and the weight average molecular weight was 69123. The result shows that polymerization reaction takes place to a great extent.

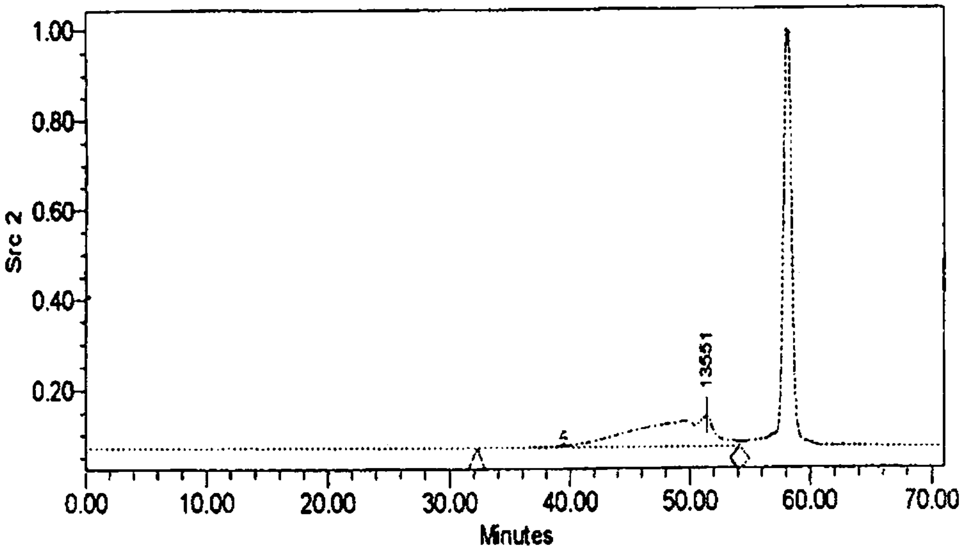


Fig.5.15 gel permeation chromatogram of the polymer

Table 5.1 GPC results

M peak	Mn	Mw	Mz	Mw / Mn	Mz / Mw
13551	25660	69123	228717	2.694	3.309

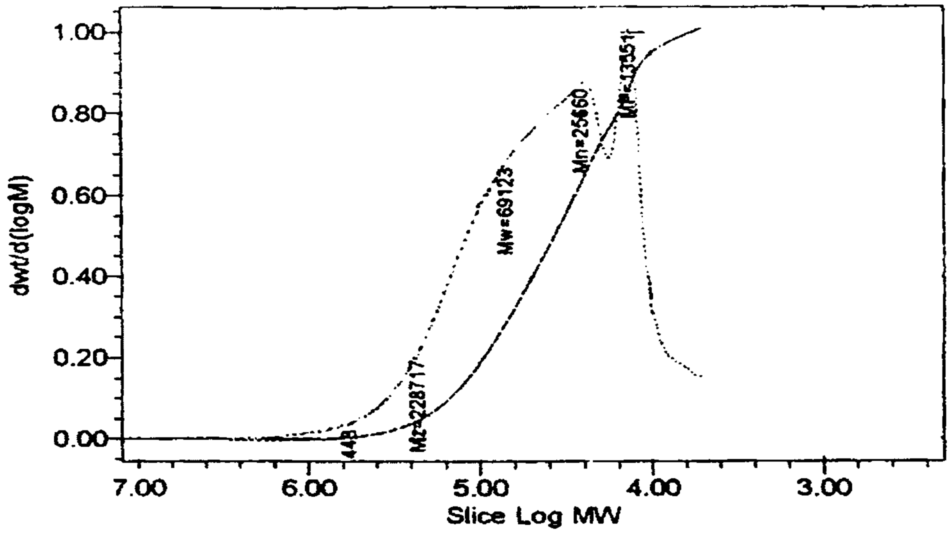
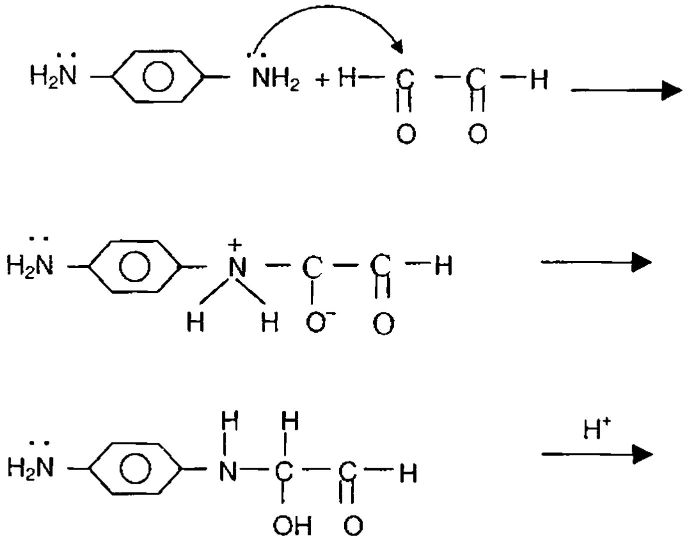
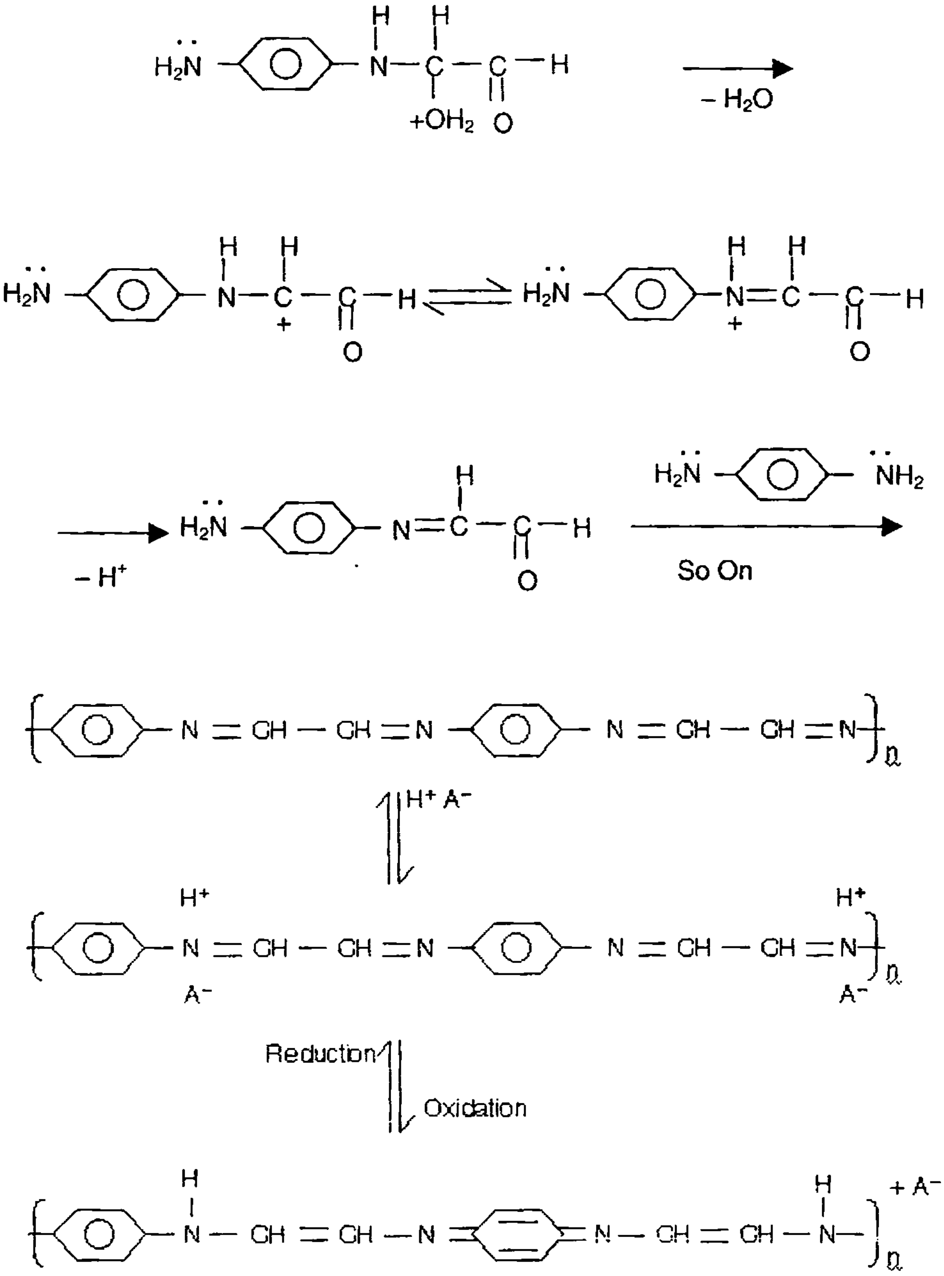


Fig.5.16 GPC distribution plot of the polymer

From the above results, the reaction between glyoxal and paraphenylene diamine to form the polymer, poly(p-phenylenediazomethine) can be represented by Scheme 5.1. Condensation reaction took place between p-phenylene diamine and glyoxal by the elimination of water molecule, forming a C= N bond .





Scheme 5.1

5.5.4 TGA

In the thermo gravimetric analysis of the sample prepared in DMF (fig.5.17), there was about 10% weight loss at 300^{0}C and about 20% weight loss at 400^{0}C and as the temperature was increased, there was continuous weight loss. The initial weight loss may be due to volatilization of water molecules and the weight loss at high temperature was related to the degradation of the polymer backbone due to the production of gases such as acetylene and ammonia. Thermo gravimetric analysis of the sample prepared in m-cresol is shown in Figure 5.18. Compared to the sample prepared in DMF, about 25% weight loss existed at 300^{0}C and about 50% weight loss at 400^{0}C occurred for this sample. This may be due to the thermal decomposition of the polymer similar to that prepared in DMF.

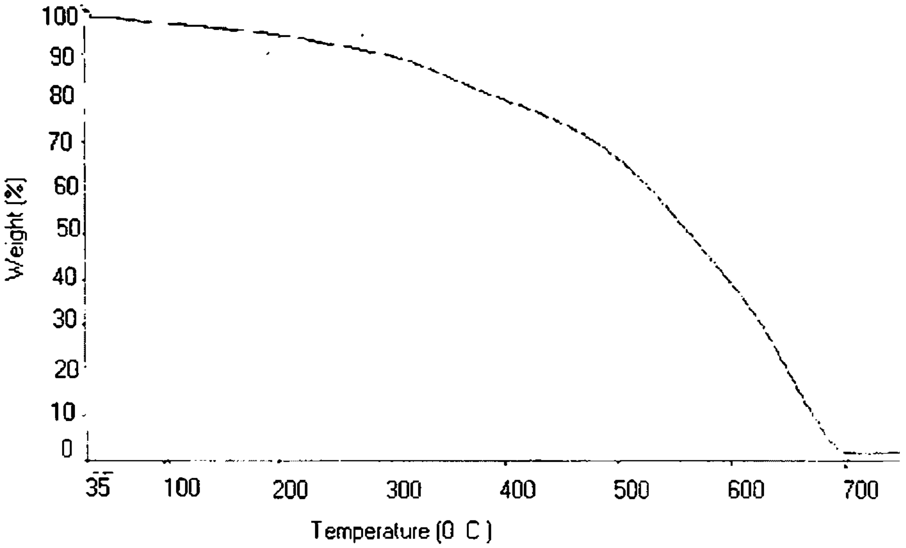


Fig.5.17 TGA of the polymer prepared in DMF

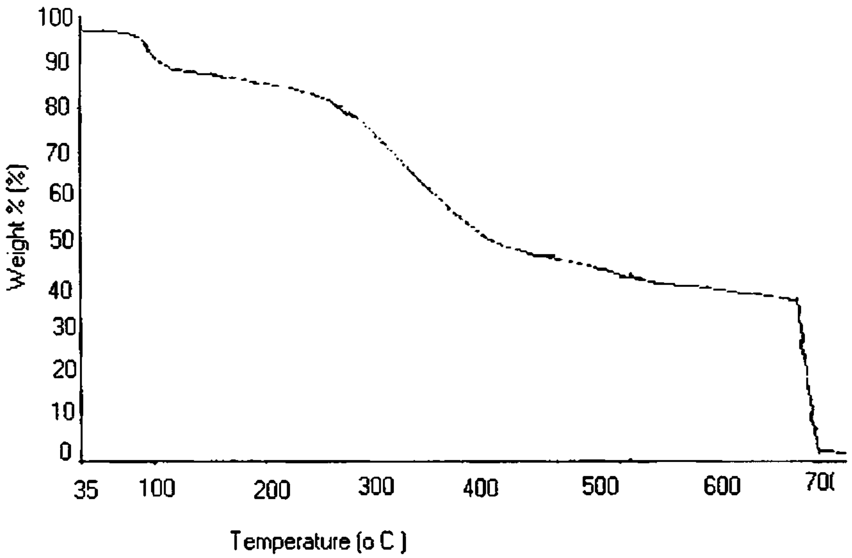


Fig. 5.18 TGA of the polymer prepared in m-cresol

5.5.5 D.C. Conductivity

The d.c. conductivity and density of the prepared samples are given the Table 5. 2. Conductivity of the undoped samples was changed with the solvent in which the reaction was carried out. The variation in conductivity may be due to tne difference in the degree of polymerization in different solvents. The conductivity of the sample prepared in DMF was greater than other samples. DMF is a polar aprotic solvent and the polymer formed were more soluble in DMF than in toluene and methanol, that helped to increase the degree of polymerization, which in turn increased the conjugation length and hence the conductivity was increased. In methanol and toluene, precipitation of the product takes place easily and hence further reaction may not take place. So the conductivity is very low in the samples prepared in methanol and toluene. The conductivity of the undoped sample prepared in m-cresol is similar to that prepared in DMF.

Table 5.2 Density and conductivity of poly(p-phenylenediazomethine) prepared in different solvents

Solvent	Density (g cm^{-3})	Conductivity(S/m)			
			Dopants		
		Undoped	HCl	$HClO_4$	I_2
DMF	1.0906	1.164×10^{-4}	8.604×10^{-2}	2.801×10^{-3}	1.019×10^{-3}
m-Cresol	0.7096	2.415×10^{-5}	3.663×10^{-2}	6.061×10^{-3}	4.082×10^{-5}
Toluene	1.1309	6.25×10^{-6}	2.463×10^{-4}	9.709×10^{-3}	9.009×10^{-4}
Methanol	1.1432	3.597×10^{-8}	2.198×10^{-5}	8.422×10^{-5}	3.086×10^{-5}

The conductivity of the doped samples was more than that of the undoped samples. This was because, after doping, more charge carriers were introduced into the polymer chain, which helped to increase the conductivity. Conductivity of acid doped samples was more than that of I_2 doped samples. This may be due to the attachment of H^+ ions to the N atom of the polymer using the lone pair of electrons, which results in the oxidation of the polymer chain. Charge delocalisation on the polymer chain helped to increase the conductivity, which was evident from the IR spectra of acid doped samples (Fig.5.12, 5.13). The low conductivity of the I_2 doped samples may be due to the fact that the oxidation of the polymer chain by iodine was very low. Also, on drying the samples, the action of heat and vacuum may be removing the iodine easily. This observation was verified by measuring the conductivity of the doped samples after one week. After one week, the conductivity of I_2 and HCl doped samples were decreased very much, while the conductivity of $HClO_4$ doped samples remained almost the same as given in Table 5.3. So $HClO_4$ was the better doping agent for poly(p-phenylenediazomethine).

Table 5.3 **Conductivity of poly(p-phenylenediazomethine) prepared in DMF**

Doping agent	conductivity (S/m)	Conductivity after one week(S/m)
HCl	8.604×10^{-2}	6.855×10^{-4}
$HClO_4$	2.801×10^{-3}	1.825×10^{-3}
I_2	1.019×10^{-3}	1.242×10^{-4}

The conductivity of the samples doped with different dopants depends on the nature of the counter ion also. Small nucleophilic counter ions appear to bind tightly to the chain, thus limiting the mobility of the charge, and larger, delocalized counter ions have a more diffuse charge and do not associate highly with the polymer chain[25]. Thus, in perchloric acid doped samples, the larger ClO_4^- counter ion helped to increase the conductivity.

5.5.6 Thermal diffusivity

Thermal diffusivity of the polymer samples prepared in different experimental conditions is given in Table 5.4. The thermal diffusivity of poly(p-phenylenediazomethine) prepared in m-cresol solvent was very high and it was in between that of Al and Fe. So poly (p-phenylenediazomethine) was a good conductor of heat.

5.5.7 Dielectric parameters

Figures 5.19- 5.21 show the variation in the dielectric constant, dielectric loss factor, and microwave conductivity of poly(p-phenylenediazomethine) prepared in different solvents at the microwave frequency of 2.17 GHz at 25°C. The microwave conductivity was less than that of a conductor, but greater than that of an insulator at microwave frequencies. Because of this property, it can be used to construct microwave components like filters.

Table 5.4 Thermal diffusivity of poly(p-phenylenediazomethine) prepared in different solvents

Solvent	Thermal diffusivity ($cm^2 s^{-1}$)
Methanol	0.0536
Toluene	0.0368
DMF	0.5037
m-Cresol	0.5088

The real part of the complex permittivity, i.e., dielectric constant of the material was increased when they were doped with HCl and $HClO_4$. On doping, due to the presence of additional charge carriers, and their movement were restricted in the polymer chain, local accumulation of charge will induce its image charge on an electrode and give rise to interfacial polarization. So dielectric constant was increased on doping, as shown in the figure 5.19. Dielectric constant of the material doped with $HClO_4$ was more than that of undoped and HCl doped samples. This may be due to the effect of introducing more charge carriers, because, $HClO_4$ is a strong oxidizing agent than HCl.

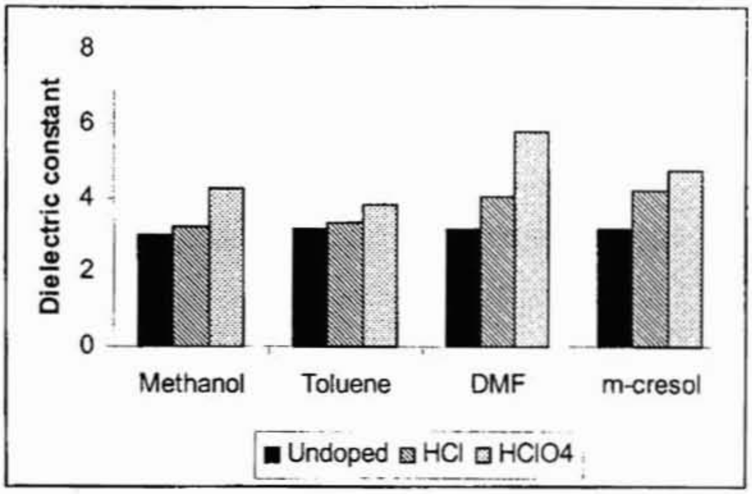


Fig. 5.19 Dielectric constant of poly(p-phenylenediazomethine) prepared in different solvents

Figure 5.20 shows the variation in the imaginary part of the complex permittivity, i.e., dielectric loss factor of different doped and undoped samples. Imaginary part of the complex permittivity or the dielectric loss factor, ε_r'' is a direct function of relaxation process and the origin of this relaxation is due to the local motion of polar groups. Dielectric loss factor of the material was increased on doping except for the polymer prepared in methanol. The increase in dielectric loss factor may be due to the increase in the polarity of the molecule on doping. For the large molecule, the rotary motion of the molecules was not sufficiently rapid for the attainment of equilibrium with the field. So more time was required for the dipole to reorient, and hence dielectric loss factor was increased. For the polymer prepared in methanol, the molecular weight of the polymer was very low due to the precipitation of the product, and the reaction was carried out at room temperature. So the time for the molecule to reorient with the field was low and hence on doping, the dielectric loss factor was decreased. Microwave conductivity is a direct function of dielectric loss factor. Hence, the increase in conductivity on doping was due to the increase in dielectric loss factor of the material as shown in the figure 5.21.

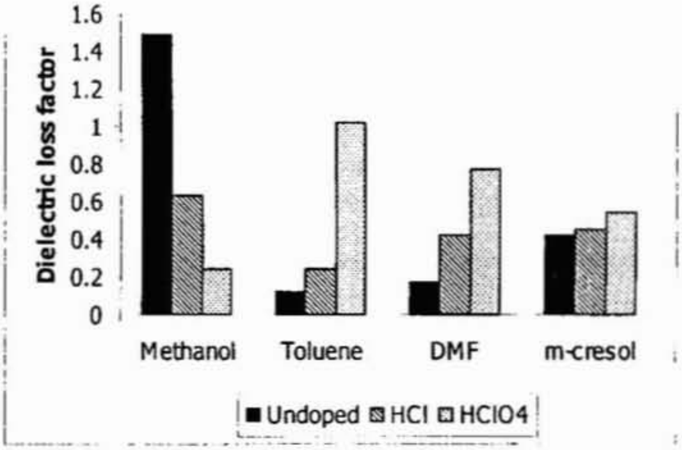


Fig. 5.20 Dielectric loss factor of poly(p-phenylenediazomethine) prepared in different solvents

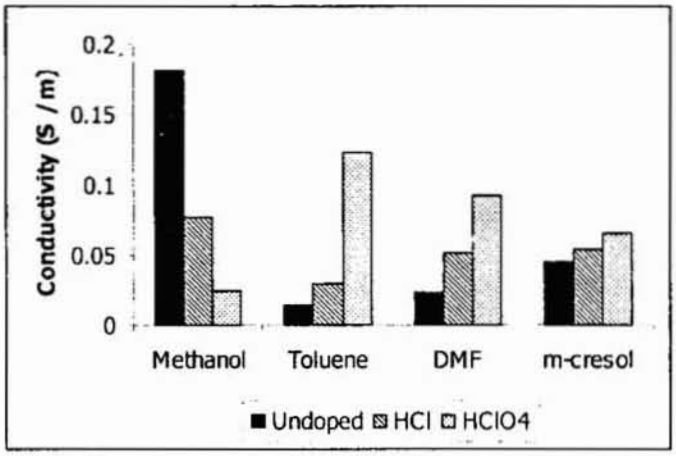


Fig. 5.21 Microwave conductivity of poly(p-phenylenediazomethine) prepared in different solvents

5.6 Conclusions

1. Condensation reaction took place between glyoxal and p-phenylene diamine to form the conducting polymer poly(p-phenylenediazomethine).
2. The molecular weight of the polymer prepared in m-cresol solvent was, Mn = 25660 and Mw = 69123.
3. The polymer was thermally stable up to about 400^0C.
4. D.C. Conductivity of the polymer prepared in DMF was more than that of other samples prepared in m-cresol, methanol and toluene.
5. Doping increased the d.c. conductivity of the polymers prepared by the condensation reaction between glyoxal and p-phenylene diamine.
6. $HClO_4$ was a better doping agent for poly(p-phenylenediazomethine) compared to HCl and I_2
7. Thermal diffusivity of the polymer was in between that of Al and Fe. So it was a good conductor of heat.
8. Dielectric properties like dielectric constant, dielectric loss and microwave conductivity increased on doping with HCl and $HClO_4$.

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Chapter 6

PREPARATION AND CONDUCTIVITY STUDIES OF BLENDS OF CONDUCTING POLYMER WITH POLYETHYLENE, POLY (VINYLCHLORIDE) AND SILICA

6.1 Introduction

The electrically conducting polymers such as polypyrrole, polythiophene, polyfuran and polyaniline have been examined for possible electronic and chemical applications[1-3]. However, the use of electrically conducting polymers has been limited in the past by problems associated with poor environmental stability and/or poor mechanical properties[4-6]. As the interchain electron transfer interactions of conjugated polymers are relatively strong compared to the Vander Waals and hydrogen bonding typical of saturated polymers, the conducting polymers tend to be insoluble and infusible. 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[7-9]. In most of these applications, the main concern is to obtain sufficient level of conductivity in the material.

This chapter reports our investigations done for obtaining conducting polymer blends. Preparation of blends, composites and interpenetrating network has been widely used as an approach to combine electrical conductivity with desirable mechanical strength of polymers[10]. Three principal approaches have been reported for increasing the processability of conducting polymers- (1) polymerising appropriately substituted monomers so that the conducting polymers become soluble and still retain substantial conductivity, (2) Preparing the polymer in dispersion form and (3) polymerising the monomers of the respective conducting polymer inside the matrices of conventional polymers leading to composite films[5].

Several attempts have been described to produce conducting polymer composites with better physical properties by either chemically or electrochemically[11-15]. Several composites of conducting polymers have been prepared for the simple reason of having polymers with good thermal and physical characteristics[16-22]. Charge transport mechanism in conducting polymer composites was reported by Radhakrishnan et.al.[23].

In-situ polymerization of glyoxal and p-phenylenediamine was done in different solvents containing different amounts of PE, PVC, and silica. The d.c. conductivity and microwave conductivity of each sample was measured. The effect of dopants like $HClO_4$, HCl and I_2 on conductivity was also studied.

6.2 Experimental

6.2.1 Materials used

Paraphenylene diamine, Glyoxal hydrate (trimer), Polyethylene, Polyvinylchloride, Ultrafine silica, N,N-Dimethyl formamide , Toluene , Tetrahydrofuran, Methanol , Acetone, Hydrochloric acid, Perchloric acid , Iodine, and Carbon tetra chloride were used in the present investigation conforming to the specifications given in Chapter II.

6.2.2 Synthesis of poly (p-phenylenediazomethine) –Polyethylene conducting polymer blends

Polyethylene (5g) was dissolved in 400 ml of toluene by gentle heating along with continuous mechanical stirring. 0.1mole of p-phenylene diamine was added to it and was dissolved in it by stirring. Then 0.1 mole of glyoxal was added and stirred well. Then the temperature of the reaction medium was increased slowly to boiling, with continuous stirring, and was refluxed at the boiling temperature for 5 hours. By that time, the precipitation of the product takes place. It was then allowed to cool to room temperature. Excess of toluene was allowed to evaporate until the precipitation of polyethylene started and then poured into excess of ice-cold water. It was allowed to settle, filtered, washed with plenty of water until the filtrate was colorless. Then it was washed with methanol, and allowed to dry at room temperature in air for one day. Then the final drying of the sample was done at 70^0C in vacuum.

The same procedure was repeated by varying the amount of polyethylene in the reaction mixture. The dried samples were powdered well in a mortar and then pelletized for the measurements. For the spectral and thermal studies, the sample was extracted with acetone until the extract was colorless, and dried well.

6.2.3 Synthesis of poly(p-phenylenediazomethine) –Polyvinylchloride conducting polymer blends

PVC (5g) was dissolved in 50 ml of Tetrahydrofuran. 0.1mole of p-phenylene diamine was added to 300 ml of N,N-dimethylformamide and was dissolved in it by stirring. Then 0.1 mole of glyoxal was added to it and stirred well. The solution of PVC in THF was added to the above reaction mixture and stirred well. Then the temperature of the reaction medium was increased slowly to boiling, with continuous stirring, and was refluxed at the boiling temperature for 4 hours. By that time, the precipitation of the product takes place. It was then allowed to cool to room temperature and then poured into excess of ice-cold water with stirring. It was allowed to settle, filtered, washed with plenty of water until the filtrate was colourless. Then it was washed with methanol, and allowed to dry at room temperature in air for one day. Then the final drying of the sample was done at 70^0C in vacuum.

The same procedure was repeated by varying the amount of PVC. For this, 10 gm of PVC was dissolved in 100ml of THF, 15 gm of PVC was dissolved in 150ml of THF, and 20 gm of PVC was dissolved in 200ml of THF and was added to the reaction mixture containing glyoxal and p-phenylenediamine in DMF.

The dried sample was powdered well, and, pelletized for the density and d.c. conductivity measurements. For the spectral and thermal studies, the sample was extracted with acetone until the extract was colorless, and dried well.

6.2.4 Synthesis of poly(p-phenylenediazomethine) –silica conducting polymer composites

0.1mole of p-phenylene diamine was added to 300 ml of DMF and was dissolved in it by stirring. 5 gm of ultrafine silica was added to it and stirred well. Then 0.1 mole of glyoxal was added to it and stirred well. Then the temperature of the reaction medium was increased slowly to boiling, with continuous stirring, and was refluxed at the boiling temperature for 4 hours. By that time, the precipitation of the product takes place. It was then allowed to cool to room temperature and then poured into excess of ice-cold water with stirring. It was allowed to settle, filtered, washed with plenty of water until the filtrate was colourless. Then it was washed with methanol, and allowed to dry at room temperature in air for one day. Then the final drying of the sample was done at 70^{0}C in vacuum.

The same procedure was repeated by varying the amount of silica to the reaction mixture containing glyoxal and p-phenylenediamine in DMF.

The dried sample was powdered well, and, pelletized for the density and d.c. conductivity measurements. For the spectral and thermal studies, the sample was extracted with acetone until the extract was colorless, and dried well.

6.2.5 Doping

1g each of the sample was added to 50ml each of 1M HCl solution, 1M $HClO_4$ solution and saturated solution of I_2 in CCl_4 and kept for 24 hours. Then it was filtered, washed with a little amount of acetone and dried at 70^0 C in dynamic vaccum for one hour.

6.3 Measurements

6.3.1 IR spectra

Particles of the polymer samples were flattened by means of cold compression between two diamond windows. IR spectra of the samples were recorded with a Biorad UMA 500infrared microscope, which is coupled to a Biorad FTS 6000 spectrometer. Spectra were recorded with a resolution of 4 cm $^{-1}$ co-adding 100 scans.

6.3.2. D.C. conductivity

D.C. conductivity of the pressed pellets was determined by the two-probe technique. The samples were sandwiched between two copper electrodes and a constant voltage (6V) was applied to the sample. The current flowing through the sample was measured using a digital multimeter (APLAB model 1087). The conductivity of the sample was calculated using the equation, $\sigma = t / RA$, where 't' is the thickness of the pellet, 'R' is the resistance of the sample ($R = E / I$, where 'E' is the applied voltage and 'I' is the resulting current through the sample), and 'A' is the area of cross section of the pellet ($A = \pi r^2$, where 'r' is the diameter of the pellet).

6.3.3 Density

Density of the pressed pellets were determined using the equation, $D = M/V$, where 'M' is the mass of the pellet and 'V' is the volume of the pellet .

6.3.4 Microwave conductivity and Complex permittivity

The dielectric properties and conductivity of the samples were measured using cavity perturbation technique[24]. The measurements were done at a microwave frequency of 2.17 GHz at room temperature (25°C).

In microwave studies the conductivity can be calculated using the equation,

Conductivity ,$\sigma = 2\pi f_s \varepsilon_0 \varepsilon_r''$

where 'f_s' is the resonant frequency, ε_0 is the complex permittivity of free space and ε_r'' is the imaginary part of the complex permittivity , which is given by the equation,

$\varepsilon_r'' = (V_c / 4V_s)(Q_t - Q_s / Q_t Q_s)$

where,' V_c ' is the volume of cavity, V_s is the volume of sample, Q_s is the quality factor of the cavity loaded with the sample and Q_t is the quality factor of the cavity with the empty sample holder.

The real part of the complex permittivity ε_r' is usually known as dielectric constant of the material. It can be calculated from the equation,

$$\varepsilon_r' = 1 + (f_t - f_s)/\, 2f_s\, (V_c/V_s)$$

where f_t =resonant frequency of the unloaded cavity and f_s is the resonant frequency of the cavity loaded with the sample.

6.4 Results and discussion

6.4.1 Poly(p-phenylenediazomethine)-polyethylene blends

Fig.6.1 gives the IR spectrum of the conducting polymer composites with polyethylene.

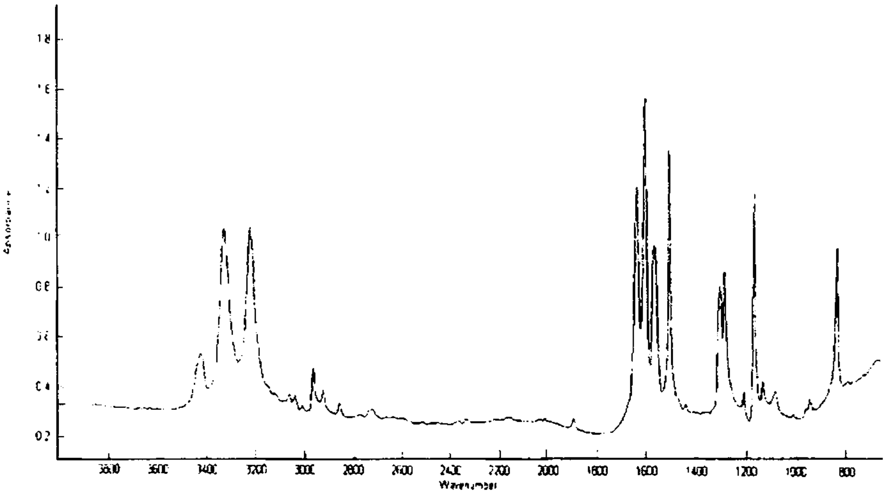

Fig. 6.1 IR spectrum of the conducting polymer-polyethylene blend

The spectral bands at 2918 and 2851cm^{-1} were characteristic of polyethylene. Other spectral bands were due to the conducting polymer. Unreacted p-phenylene diamine was also present in the sample. The bands at 3328, 3221,1855, 1639, and 1130cm^{-1} were due to unreacted p-phenylene diamine. Fig.6.2 compares the IR spectrum of the polymer with the blend. The intensity of carbonyl band at 1670 cm^{-1} was very low. The two spectra were similar. From these, we can conclude that conducting polymer was incorporated into the polyethylene matrix. By the action of temperature, and pressure, we can convert these blends into sheet form. So the processability of the conducting polymer can be improved by making its blend with polyethylene without any chemical change in the polymer structure.

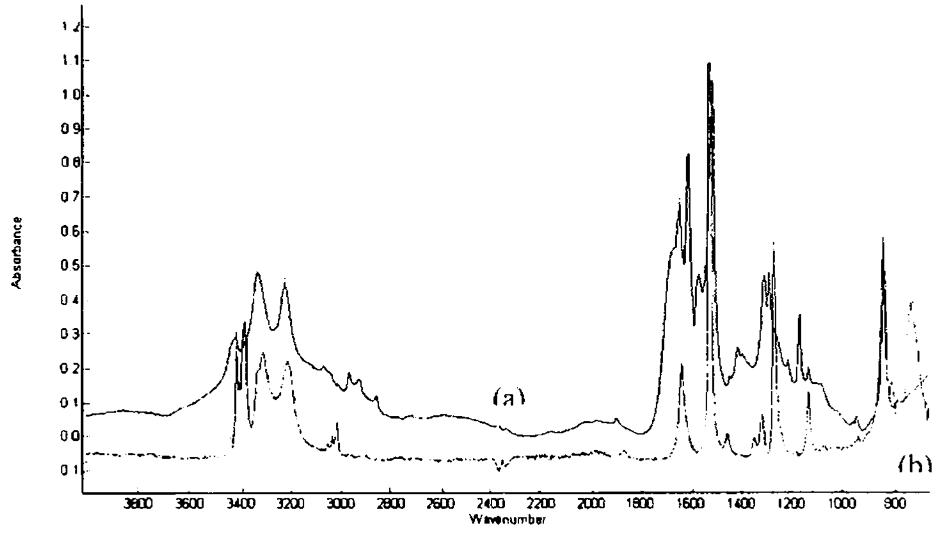

Fig. 6.2 IR spectra of (a) conducting polymer prepared in toluene and (b) its polyethylene blend

Figures 6.3 and 6.4 shows the IR spectra of the conducting polymer blend doped with HCl and $HClO_4$ respectively.

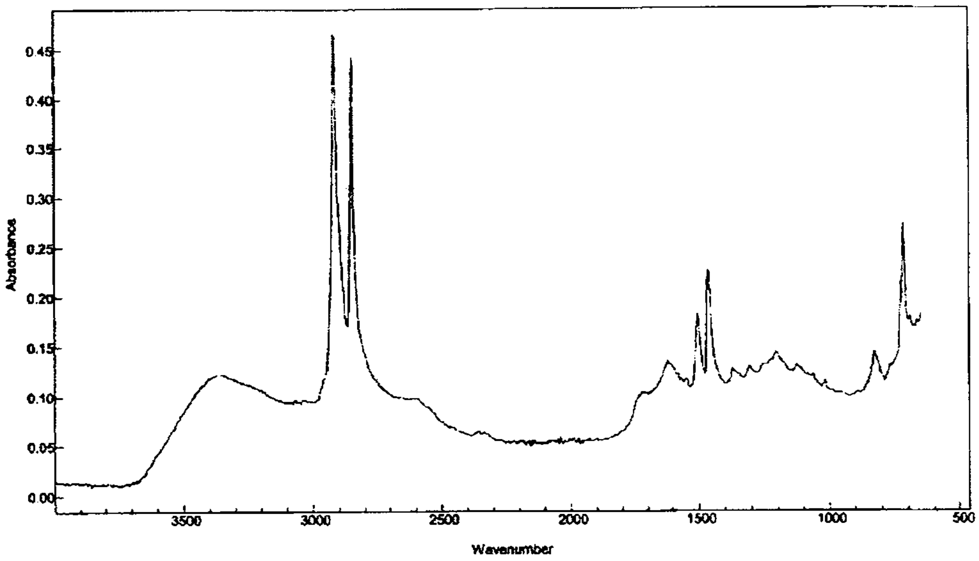

Fig. 6.3 **IR spectrum of the conducting polymer-polyethylene blend doped with HCl**

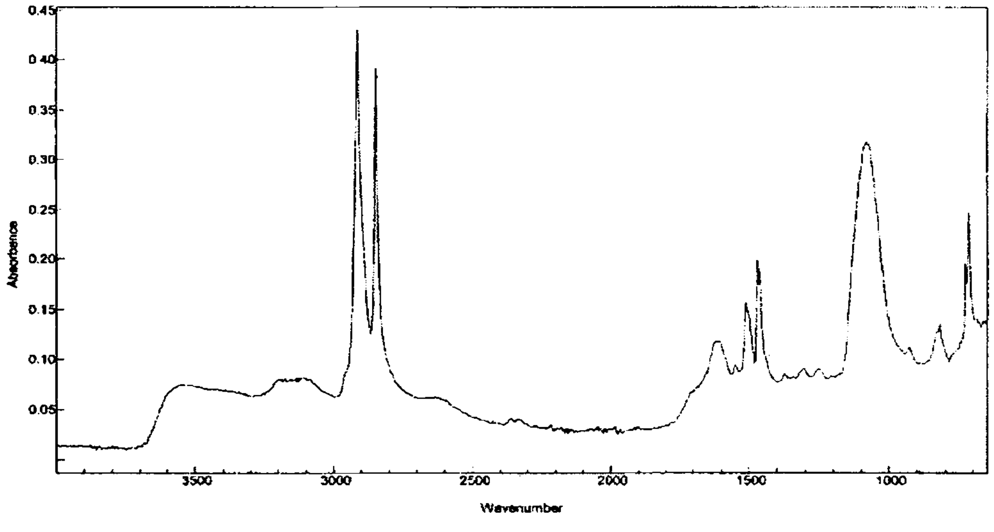

Fig. 6.4 **IR spectrum of the conducting polymer-polyethylene blend doped with $HClO_4$**

The absorption bands at 3325, 3219, and 1637 cm^{-1} of unreacted p-phenylene diamine were disappeared on doping. This was because, on treating the blend with acids, unreacted p-phenylene diamine dissolved in it and was removed on filtration. The absorption band at 3419 cm^{-1} in the undoped blend was shifted to a broad band at 3336 cm^{-1} and 3537 cm^{-1} due to protonation, in HCl and $HClO_4$ doped samples respectively. Strong bands at 2914 and 2845 cm^{-1} were due to PE. The bands at 1508 and 1463 cm^{-1} were due to benzenoid and quinoid ring attached to N atom respectively. The very weak peak at 1050 cm^{-1} was due to HCl dopant and the strong peak at 1080 cm^{-1} was due to $HClO_4$ dopant. Other absorption bands were the same as that in the undoped sample.

Figure 6.5 shows the density of the blends of the conducting polymer based on glyoxal, p-phenylene diamine and varying amounts of polyethylene.

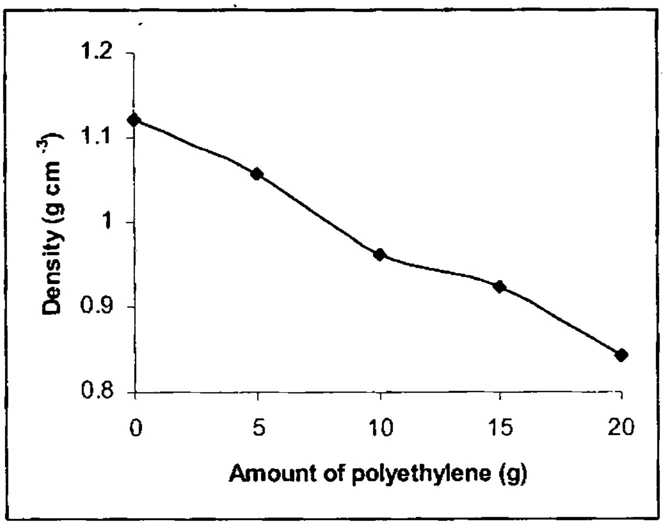

Fig. 6. 5 Density of the conducting polymer-polyethylene blends

The density of the blends were lower than that of poly(p-phenylenediazomethine). It was because; the density of polyethylene was lower than that of the polymer prepared in toluene solvent. The density of the blends was decreased with increase in the amount of polyethylene in the blend.

The d.c. conductivity of the blends was decreased with increase in the amount of polyethylene as given in figure 6.6. It was because, polyethylene is an insulator and the presence of polyethylene in the composite prevented the free movement of electrons through the conducting polymer chain.

The conductivity of the doped samples was more than that of the undoped samples. This was because, after doping, more charge carriers were introduced into the polymer chain, which helped to increase the conductivity. Conductivity of perchloric acid doped samples was more than that of other doped samples. This may be due to the attachment of H^+ ions to the N atom of the polymer using the lone pair of electrons. Oxidation of the polymer chain takes place and the electron transfer occurs between the polymer chain and through the polymer chain. Conductivity of the I_2 doped samples were lower than that of samples doped with HCl and $HClO_4$.

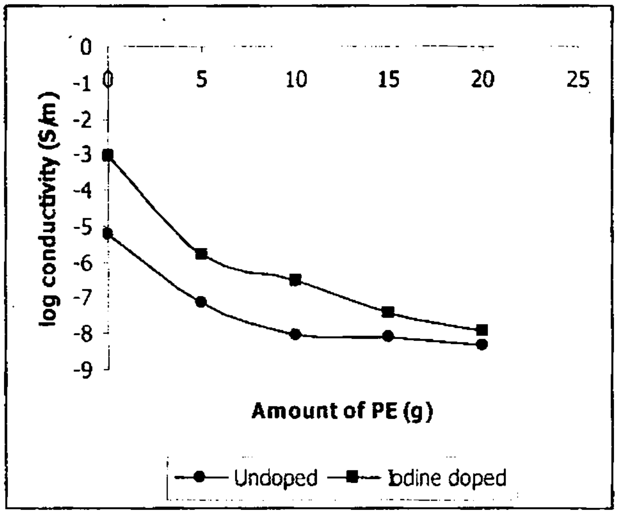

Fig. 6. 6 Conductivity of the undoped and iodine doped polyethylene blends

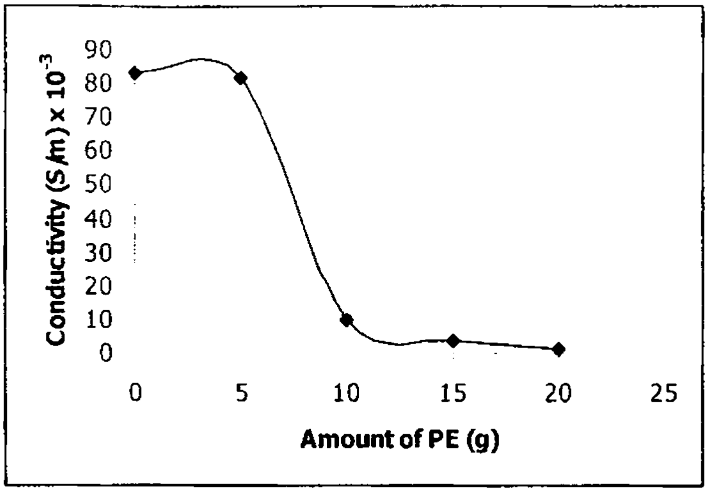

Fig. 6. 7 D.C. conductivity of the conducting polymer/polyethylene blends doped with $HClO_4$

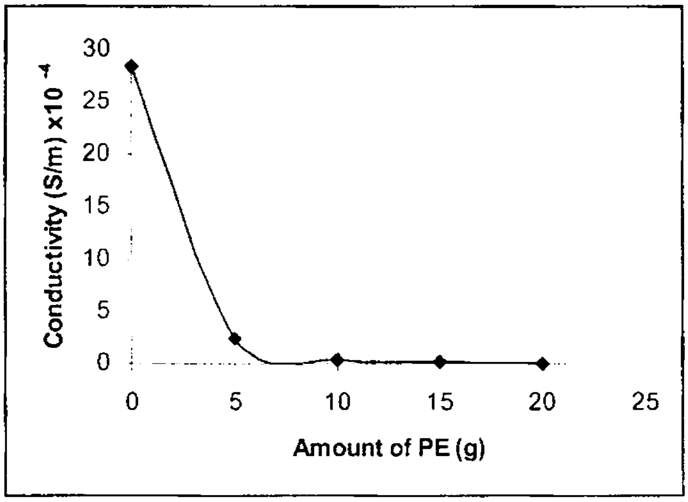

Fig. 6. 8 D.C. Conductivity of the conducting polymer/polyethylene blends doped with HCl

It may be due to the fact that the binding force between iodine and polymer chain was very low. Also, on drying the samples, the action of heat and vacuum may be removing the iodine easily, compared to HCl and $HClO_4$[25]. This observation was verified by measuring the conductivity of the doped samples after one week as reported in Chapter V. $HClO_4$ was found to be the better doping agent. It was because, the size of ClO_4^- counter ion is large, compared to Cl^- ion and so the H^+ ions were more tightly attached to the polymer chain. Hence the removal of the dopant was not occurring readily. The stability of the $HClO_4$ dopant was also evident from the IR spectra. The intensity of the absorption band due to $HClO_4$ was more, while that of HCl was very weak.

6.4.2 Poly(p-phenylenediazomethine)-polyvinylchloride blends

Figure 6.9 gives the IR spectrum of the conducting polymer blends with PVC. A broad band existed between 3200 and 2400 cm^{-1}. These bands can be assigned to the $-(N\text{-}H_x)\text{-}Cl$ strtetching vibration of amine salts. Other spectral bands were due to the conducting polymer. Some more absorption bands can be ascribed to the PVC spectrum. Figure 6.10 compares the IR spectrum of the conducting polymer with that of the blend. Some of the spectral bands were common in both of the spectra. From these, we can conclude that conducting polymer was incorporated into the PVC matrix.

As the amount of PVC was increased in the blends, the solubility of the polymer was increased. This may be due to the effect of two solvents, THF and DMF, in the reaction medium, or, it may be due to the removal of HCl from PVC by the action of heat during the course of the reaction. The presence of acid was found to increase the solubility of the conducting polymer. In concentrated acids, the polymer was soluble at high temperature. So the processability of the conducting polymer can be improved by making its blends with PVC without any chemical change in the polymer structure.

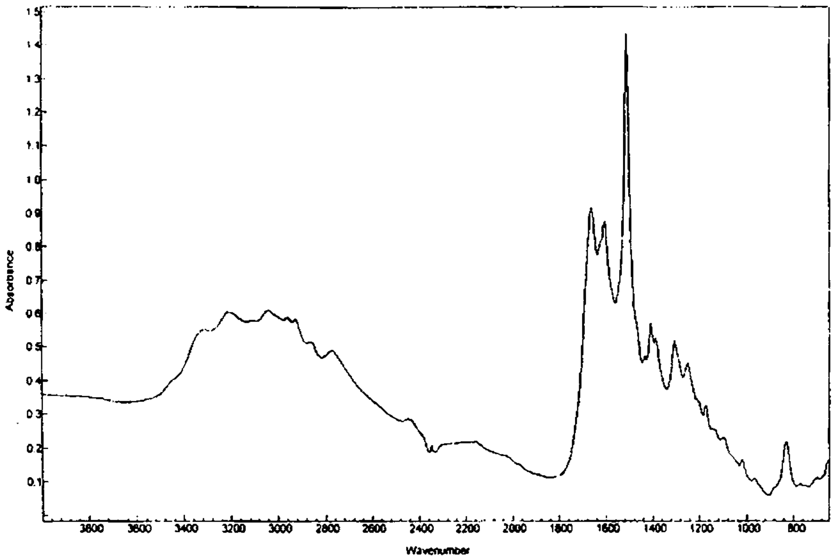

Fig. 6.9 IR spectrum of the conducting polymer- PVC blend

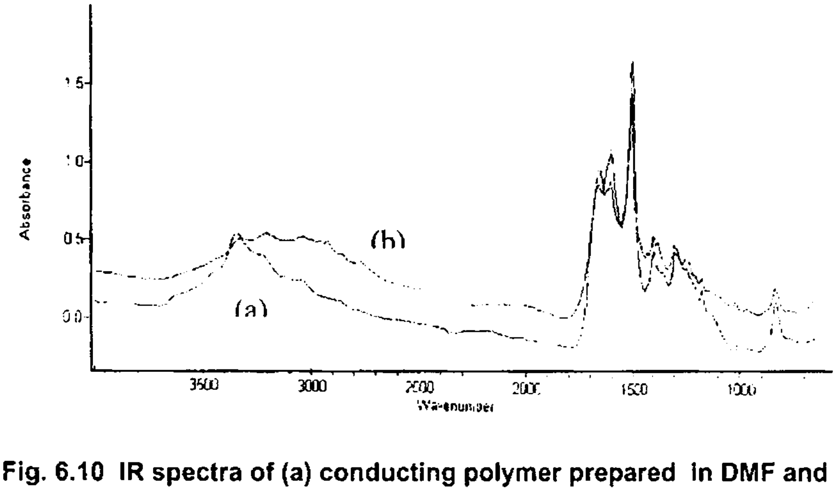

Fig. 6.10 IR spectra of (a) conducting polymer prepared in DMF and (b) its blend with PVC

Figures 6.11 and 6.12 show the IR spectra of the conducting polymer /PVC blends doped with HCl and $HClO_4$.

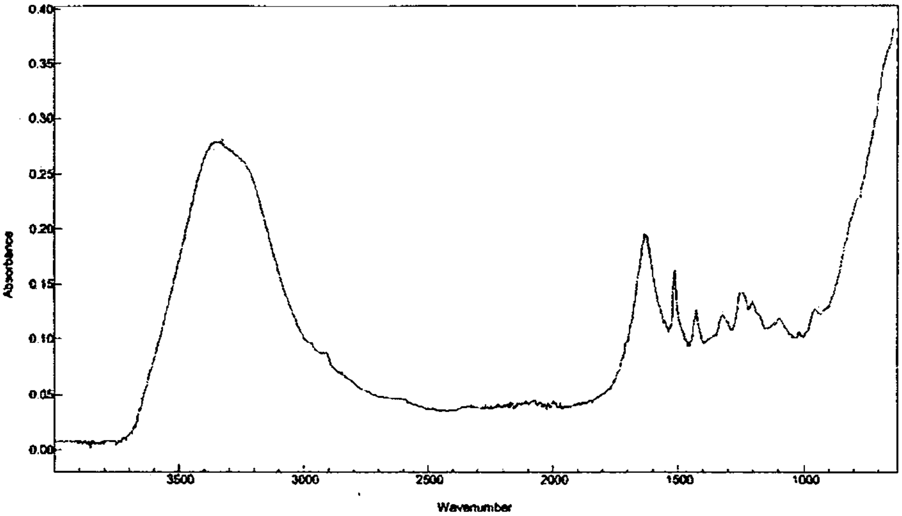

Fig. 6.11 IR spectrum of the conducting polymer/PVC blends doped with HCl

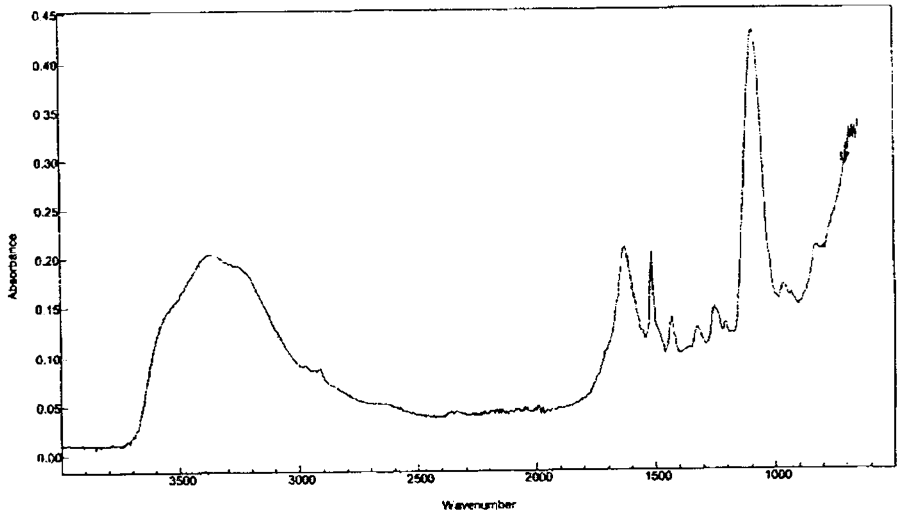

Fig. 6.12 IR spectrum of the conducting polymer/PVC blend doped with $HClO_4$

The absorption peak at 3345 cm^{-1} in the undoped polymer was shifted to a broad band in the region of 3338 and 3360 cm^{-1} in HCl and $HClO_4$ doped samples respectively. The strong peak at 1628 cm^{-1} was characteristic of C=N bond in conjugated polymers. The bands at 1094 and 1084 cm^{-1} were due to the dopant molecules HCl and $HClO_4$. The bands at 1512 and 1425 cm^{-1} showed the benzenoid and quinoid rings attached to N atom. Other bands were same in undoped and doped samples.

D.C. conductivity of the blends of the conducting polymer based on glyoxal, p-phenylene diamine and varying amounts of polyvinyl chloride is shown in the figure6.13.

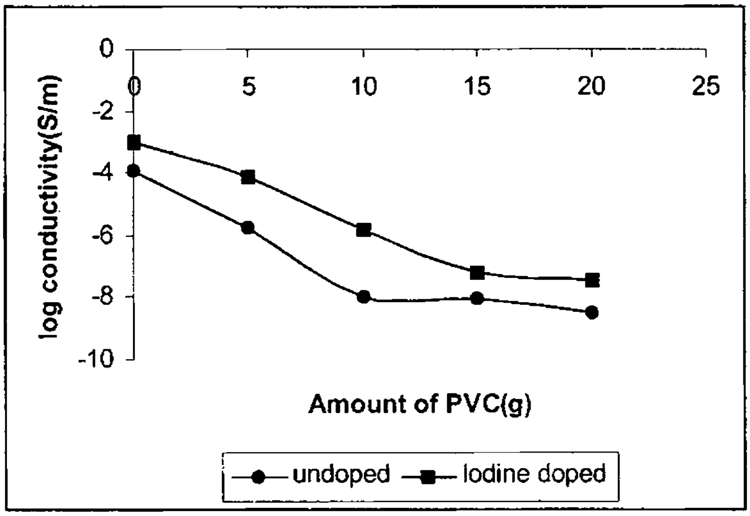

Fig. 6.13 D.C. Conductivity of the conducting polymer/PVC blends

The d.c. conductivity of the undoped blends decreased with increase in the amount of PVC. It was because, PVC is an insulator and the presence of nonconducting PVC in the composite prevented the free movement of electrons through the conducting polymer chain. Here, the conducting region was separated by a nonconducting region, so that the jumping of electrons from one conducting region to other became difficult. Hence the conductivity was decreased as in the case of polyethylene blends.

The variation in d.c. conductivity of the doped samples with the amount of PVC is given in figure.6.14.

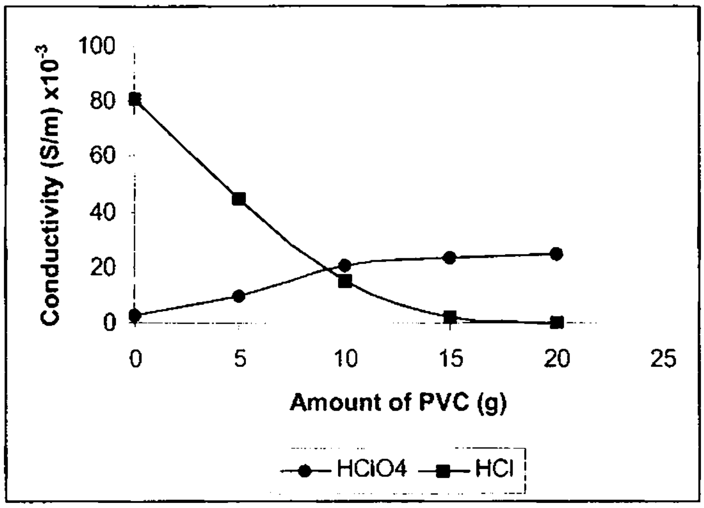

Fig.6.14 D.C. Conductivity of HCl and $HClO_4$ doped conducting polymer/ PVC blends

The d.c. conductivity of the doped samples was more than that of the undoped samples. This was because, after doping, more charge carriers were introduced into the polymer chain, which helped to increase the conductivity. Conductivity of perchloric acid doped samples containing higher amount of PVC were more than that of other doped samples. $HClO_4$ was found to be the better doping agent because, of the large size of ClO_4^- counter ion, which helped to tightly attach the dopant to the polymer chain. Hence the removal of the dopant was difficult. This may be due to the attachment of H^+ ions to the N atom of the polymer using the lone pair of electrons to increase the charge delocalization as it is clear from the IR spectra.. Conductivity of the I_2 doped samples were lower than that of other samples doped with HCl and $HClO_4$ as shown if Fig.6.13. It may be due to the fact that charge delocalization due to iodine on the polymer chain was very low. Also, on drying the samples, the action of heat and vacuum may be removing the iodine easily, compared to acid dopants.

The d.c. conductivity of perchloric acid doped blends were more than that of the pure conducting polymer doped with perchloric acid. As the amount of PVC was increased, d.c. conductivity was increased and remained almost constant at higher amount of PVC. This was because, PVC present in the blend is polar in nature, and the charge delocalization and oxidation takes place with the conducting polymer as well as with PVC molecules as shown in the IR spectra. So the removal of the dopant molecule may be difficult during the drying process and since the charge carriers were not lost, the conductivity was higher for the blends. After a saturation point was reached, the increase in conductivity was negligible because, the amount of insulating region of PVC was increased in the blend.

Dielectric properties of conducting polymer/PVC blends are given in the figures 6.15-6.17 at room temperature in the microwave frequency of 2.17 GHz. Figure 6.15 shows the variation in dielectric constant of acid doped and undoped PVC blends.

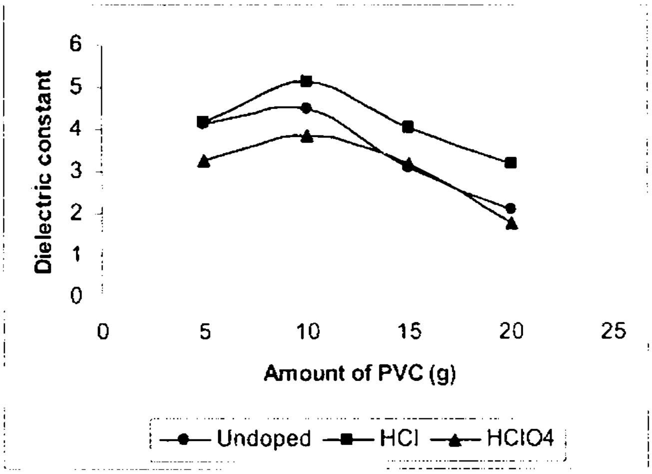

Fig.6.15 Dielectric constant of conducting polymer/PVC blends

The dielectric constant of the HCl doped blends were more than that of undoped samples. On doping, due to the presence of additional charge carriers, and their movement were restricted in the polymer chain, local accumulation of charge will induce its image charge on an electrode and give rise to interfacial polarization. Dielectric constant of $HClO_4$ doped samples were less than that of undoped samples. This may be due to orientation polarization of the dipoles caused by the alternating accumulation of charges at the interfaces between different phases of materials-i.e., between PVC and poly(p-phenylenediazomethine), even though more charge carriers were introduced. As the amount of PVC was increased, dielectric constant was increased first, up to about 10g of PVC was added in the blend. This was due to the presence of additional charge carriers, i.e., HCl eliminated from PVC, act as dopant. As the amount of PVC was increased more, dielectric constant was decreased due to the insulating effect of PVC.

Figure 6.16 shows the variation in the imaginary part of the complex permittivity, i.e., dielectric loss factor of the conducting polymer/PVC blends.

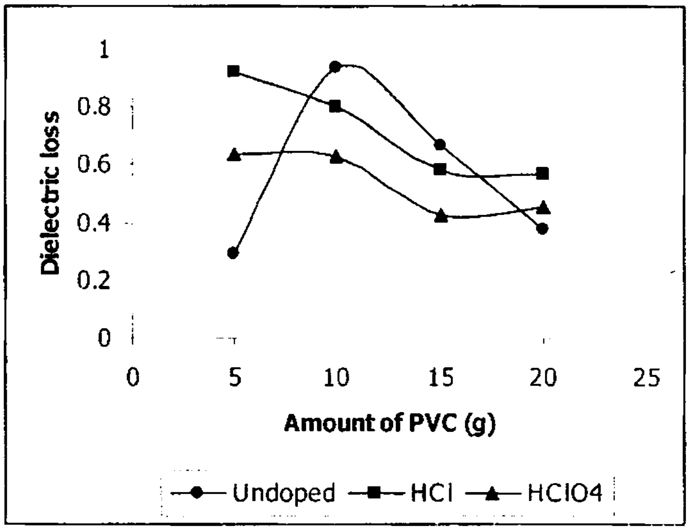

Fig.6.16 Dielectric loss factor of conducting polymer/PVC blends

As the amount of PVC was increased, dielectric loss factor of undoped material was increased first, and then decreased. The initial increase in loss may be due to the presence of polar group in PVC in which some of the HCl eliminated during the polymerization may be acting as a dopant. As the amount of PVC was increased, the insulating effect of PVC predominates, and dielectric loss factor was decreased with increase in the amount of PVC. For doped samples, the dielectric loss factor of the blends was decreased with increase in the amount of PVC. On doping, more charge carriers were introduced, and so the dielectric loss factor of the doped samples were higher than undoped sample containing lower amount of PVC. But as the amount of PVC was increased more, the insulating effect of PVC predominates, and hence dielectric loss factor was decreased.

Figure 6.17 shows the variation in the microwave conductivity of doped and undoped samples of conducting polymer/PVC blends with the amount of PVC.

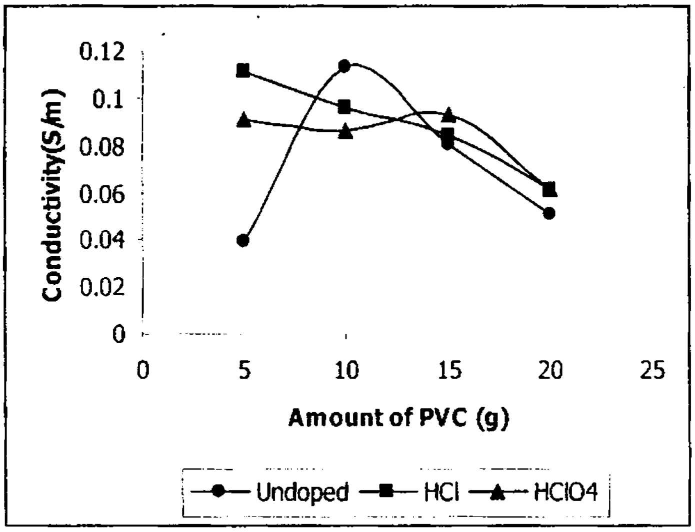

Fig.6.17 Microwave conductivity of conducting polymer/PVC blends

As the amount of PVC was increased, the microwave conductivity of undoped samples was increased first and then decreased. This was due to the initial increase and then decrease in the dielectric loss factor of the blends with the amount of PVC. Microwave conductivity is a direct function of dielectric loss. So the change in the microwave conductivity was the same as that of dielectric loss factor. For acid doped samples, the conductivity was decreased as the amount of PVC increased due to the increase in the insulating effect of PVC.

6.4.3 Poly(p-phenylenediazomethine)- silica composites

Figure 6.18 shows the IR spectrum of the conducting polymer composite with silica. The absorption bands at 1657, 1108, and 803 cm^{-1} were characteristic of silica present in the composite. Other spectral bands were due to the conducting polymer prepared in DMF. Figure 6.19 gives the comparison of the IR spectra of the conducting polymer and their composite with silica. The two spectra have many absorption bands, which were similar. The spectrum of the polymer composite had the same spectral features as that of the pure polymer.

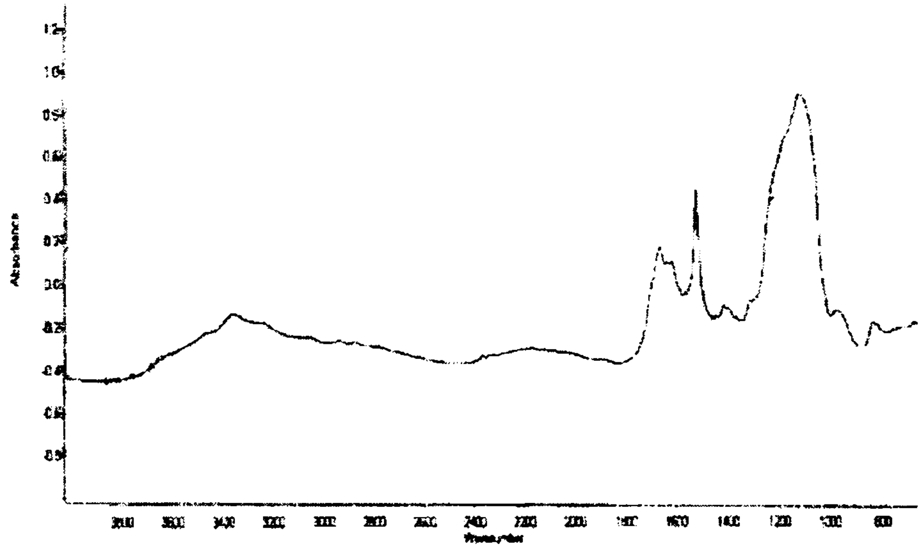

Fig. 6.18 IR spectrum of the conducting polymer- silica composite

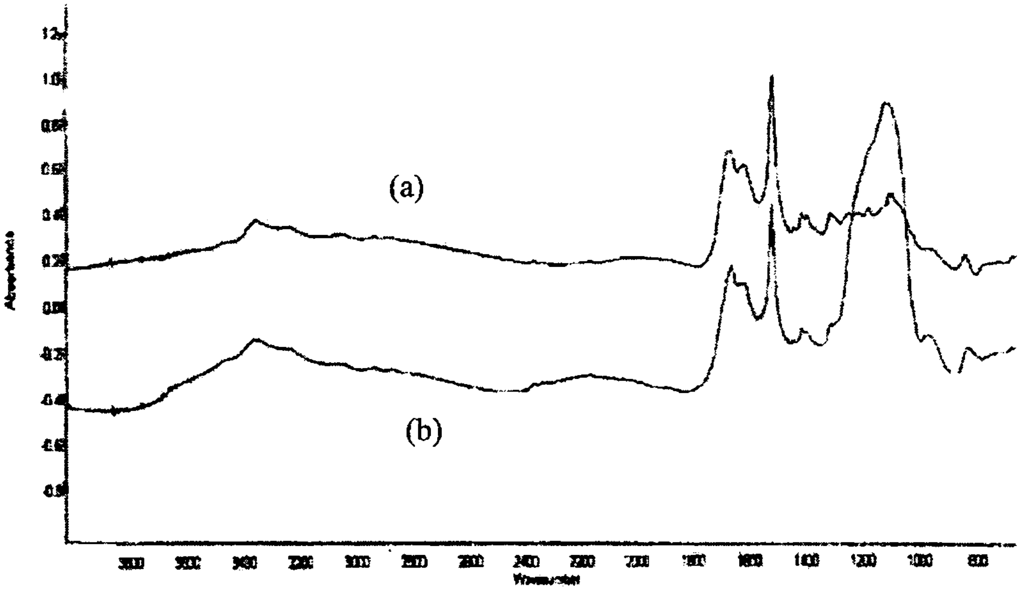

Fig. 6.19 IR spectra of (a) conducting polymer prepared in DMF and (b) it's composite with silica

IR spectra of the silica composite doped with HCl and $HClO_4$ are given in the figures 6.20 and 6.21. The absorption band 3345 cm^{-1} in the undoped polymer was shifted to a broad band in the region of 3364 and 3485 cm^{-1} in HCl and $HClO_4$ doped samples respectively. The strong peak at 1626 $cm^{-1}$was characteristic of C=N bond in conjugated polymers. The bands at 1061 and 1045 cm^{-1} was due to the dopant molecules HCl and $HClO_4$. The bands at 1508 and 1045 cm^{-1} showed the benzenoid and quinoid rings attached to N atom. Other bands were same in undoped and doped samples.

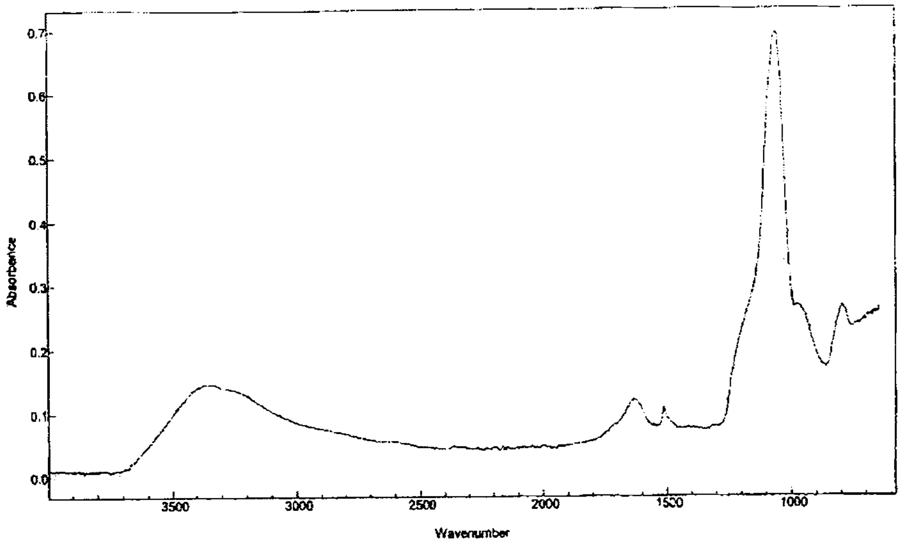

Fig.6.20 IR spectrum of the conducting polymer/ silica composite doped with HCl

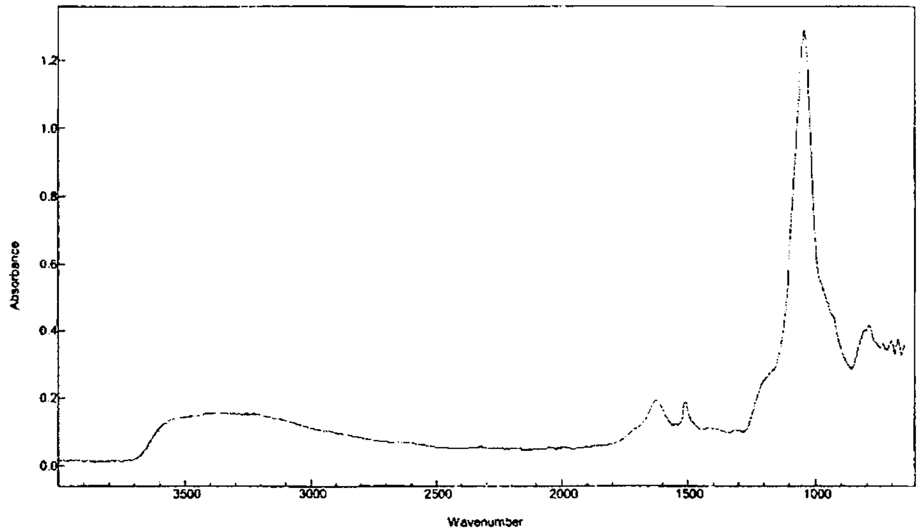

Fig.6.21 IR spectrum of the conducting polymer/silica composite doped with $HClO_4$

Figure 6.22 shows the density of the composites of the conducting polymer based on glyoxal, p-phenylene diamine and varying amounts of fine silica.

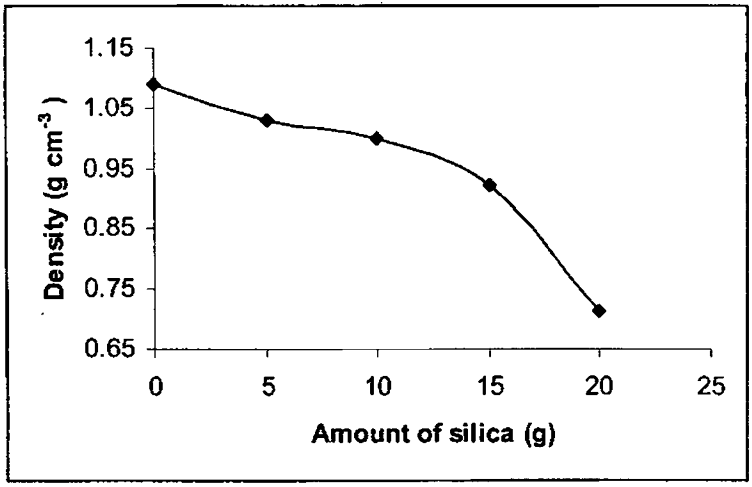

Figure 6.22 Density of the silica composites

The density of the composites were lower than that of poly(p-phenylenediazomethine). It was because; the density of silica is lower than that of the polymer prepared in DMF solvent. The density of the composites was found to decrease with increase in the amount of silica in the composite.

The d.c. conductivity of the undoped composites and iodine doped composites was decreased with increase in the amount of silica similar to the observation for the composites with polyethylene and PVC and is shown in the figure 6.23. It was because; silica, which is an insulator, prevents the free movement of electrons through the conducting polymer chain. Here also, a nonconducting region separates the conducting region, so that the jumping of electrons from one conducting region to other becomes difficult. Hence the d.c. conductivity was decreased with an increase in the amount of silica in the composite. For HCl doped samples also, conductivity decreased with the amount of silica in the composite as shown in figure 6.24.

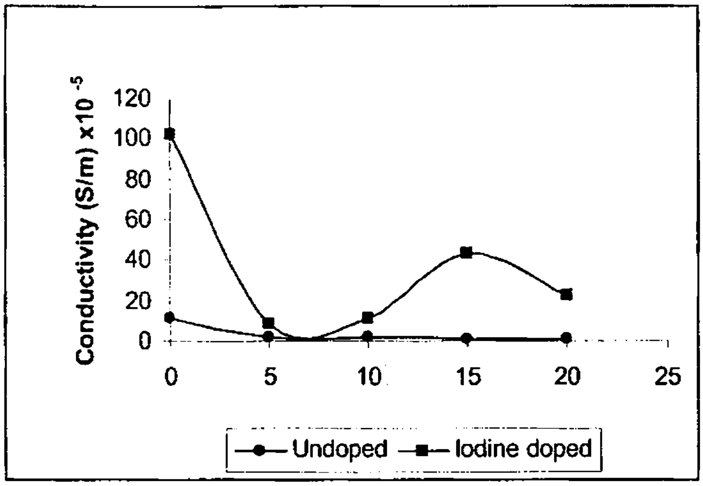

Figure 6.23 D.C.Conductivity of undoped and iodine doped conducting polymer/silica composites

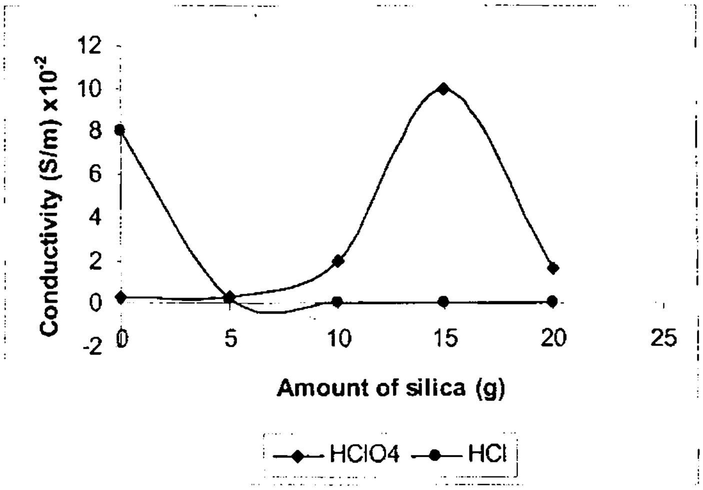

Figure 6.24 D.C. Conductivity of HCl and $HClO_4$ doped conducting polymer/silica composites

The d.c. conductivity of the doped samples was more than that of the undoped samples. This was because, after doping, more charge carriers were introduced into the polymer chain, which helped to increase the conductivity. Conductivity of perchloric acid doped samples was more than that of other doped samples. $HClO_4$ was found to be the better doping agent because, of the large size of ClO_4^- counter ion, which helped to tightly attach the dopant to the polymer chain and due to its higher oxidizing effect. Hence the removal of the dopant was difficult. This may be due to the attachment of H^+ ions to the N atom of the polymer using the lone pair of electrons. Hence charge delocalization was increased which is clear from the IR spectra. D.C.conductivity of the I_2 doped samples was lower than that of other samples doped with HCl and $HClO_4$ as in the case of PE and PVC composites.

The d.c.conductivity of perchloric acid doped composites were more than that of the pure conducting poymer doped with perchloric acid and as the amount of silica was increased, the conductivity increased first up to about 15 g of silica present in the composite. As the amount of silica was increased further, conductivity decreased due to insulating nature of silica. The conduction process can be accounted for in terms of electrons hopping between localized states under the assistance of proton transfer, for which the presence of water plays an essential role[26,27]. Silica as well as perchloric acid can adsorb water molecules and the presence of moisture increased the d.c. conductivity. Conductivity of HCl doped samples was decreased with increase in the amount of silica, due to the insulating effect of silica.

The changes in the dielectric parameters of silica composites at 2.17GHz at room temperature are given in the figures 6.25-6.27. The variation in dielectric constant for the doped and undoped samples is shown in the figure6.25. Dielectric constant of $HClO_4$ doped samples was more than that of undoped and HCl doped samples. It was due to the presence of moisture in the samples due to the hygroscopic nature of silica and $HClO_4$. Hence as the amount of silica was increased, dielectric constant was increased for $HClO_4$ doped samples. For undoped and HCl doped samples, dielectric constant was decreased with increase in the amount of silica due to the polarization caused by the alternating accumulation of charges at the interfaces between different phases of materials due to the orientation polarization of the dipoles. At higher amount of silica, the slight increase in dielectric constant may be due to the moisture present in the sample.

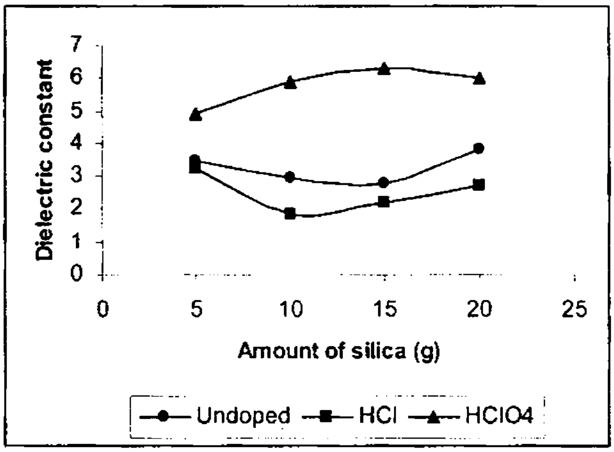

Fig. 6.25 Dielectric constant of conducting polymer/silica composites

Figure 6.26 and 6.27 shows the variation in dielectric loss factor and microwave conductivity of the silica composites. For undoped samples, dielectric loss and conductivity was decreased as the amount of silica was increased. This was due to the insulating effect of silica. For doped samples, dielectric loss factor and hence the microwave conductivity increased at first, with increase in the amount of silica, reached a maximum value, and then decreased. The increase in the values was due to the presence of moisture in the samples. At higher amount of silica, the insulating effect was predominated and hence microwave conductivity and dielectric loss factor was decreased.

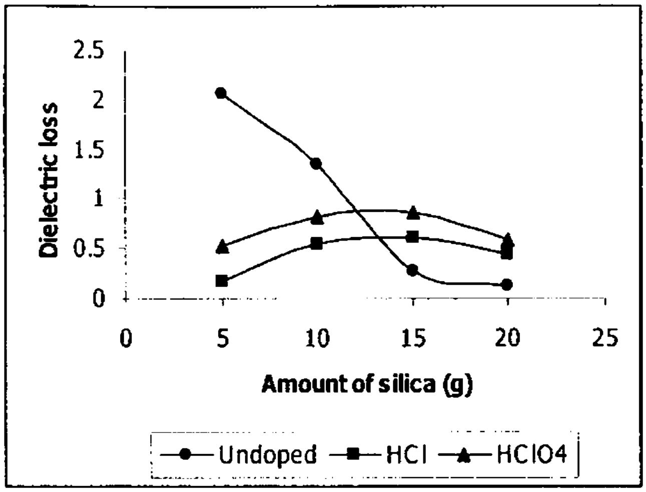

Fig. 6.26 Dielectric loss factor of conducting polymer/silica composites

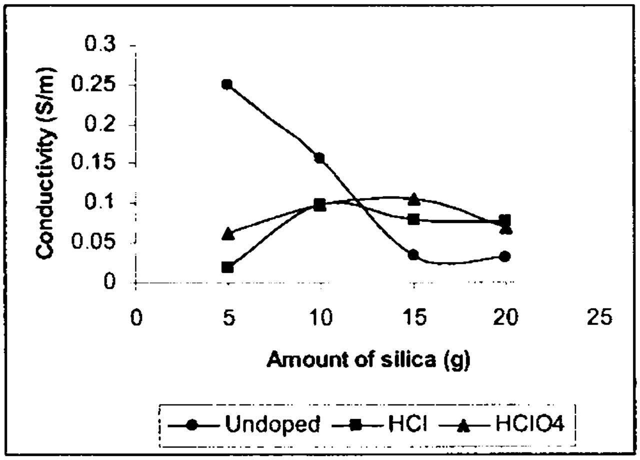

Fig. 6.27 Microwave conductivity of conducting polymer/silica composites

6.5 Conclusions

1. The d.c. conductivity of the undoped conducting polyme blends was lower than the d.c. conductivity of the conducting polymer.
2. The d.c. conductivity of the undoped polymer blends was decreased with increase in the amount of polyethylene, PVC, and silica.
3. The d.c. conductivity of the conducting polymer blends was increased on doping with HCl, $HClO_4$ and iodine.
4. The d.c. conductivity of all blends of conducting polymer with polyethylene doped with HCl, $HClO_4$ and iodine was decreased with increase in the amount of polyethylene.
5. The d.c. conductivity of the blends of conducting polymer with PVC doped with HCl and iodine was decreased with increase in the amount of PVC, but it was increased on doping with $HClO_4$ and it remained constant at higher concentration of PVC.
6. The d.c. conductivity of the composites of conducting polymer with silica doped with HCl and iodine was decreased with increase in the amount of silica, but on doping with $HClO_4$, it increased first up to about 15 g of silica content and then decreased with increase in the amount of silica.
7. On doping with HCl, the dielectric constant of the conducting polymer blend with PVC was increased. Dielectric constant was decreased when the samples were doped with $HClO_4$.
8. As the amount of PVC was increased, the dielectric constant,dielectric loss factor and microwave conductivity of undoped conducting polymer blend with PVC was increased first and then decreased and their values decreased for doped samples.
9. For silica composites,dielectric constant of $HClO_4$ doped samples was more than undoped and HCl doped samples.
10. For undoped silica composites, dielectric loss and conductivity was decreased as the amount of silica was increased. For doped samples, dielectric loss

factor and hence the microwave conductivity increased at first, with increase in the amount of silica, reached a maximum value, and then decreased.

11. As the amount of silica was increased, dielectric constant was increased for $HClO_4$ doped samples. For undoped and HCl doped samples, dielectric constant was decreased with increase in the amount of silica.
12. For undoped samples, dielectric loss and conductivity was decreased as the amount of silica was increased.
13. For doped samples, dielectric loss factor and hence the microwave conductivity increased at first, with increase in the amount of silica, reached a maximum value, and then decreased.

6.6 References

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Chapter 7

SUMMARY AND CONCLUSIONS

The primary aim of this work has been to develop conductive silicone and nitrile rubbers, which are extensively used for making conductive pads in telephone sets, calculators and other applications. Another objective of the work has been to synthesise and characterize novel conducting polymers based on glyoxal and paraphenylenediamine- poly(p-phenylenediazomethine. Conducting polymer matrices were developed from polymer blends such as poly(p-phenylenediazomethine), polyethylene, PVC and silica and their properties were studied. The contents of the various chapters in this thesis are summarised below.

An introduction about conducting polymers and conductive rubbers and their composites are given in chapter 1. The various factors affecting the conductivity and the mechanism of conduction are discussed in detail. A brief history of the synthesis of various conducting polymers is also given. The advantage of conducting polymers and conductive elastomer composites are highlighted. The objectives of the present study are also listed.

The specifications of all the materials used in the study and different experimental techniques used are described in chapter 2.

The studies on silicone rubber compounds are given in chapter 3. Silicone rubber was made conducting by the incorporation of different types of carbon blacks such as acetylene black, lamp black, HAF black and ISAF black. The effect of concentration of carbon black on the conductivity of silicone rubber was investigated. It was found that conductivity increases with the amount of blacks. The influence of particle size, structure and the type of the carbon black was studied by comparing the conductivity of different vulcanizates loaded with the same amount of different blacks. It was found that the conductivity of silicone rubber loaded with acetylene black was higher than those of other samples loaded with other carbon blacks. The effect of temperature on the conductivity of these vulcanizates was also studied in the temperature range of 25^0 C to 150^0 C. The mechanical properties such as tensile strength tear strength, hardness, elongation at break etc. of each vulcanizates were also determined. Silicone rubber was blended with high-density polyethylene and their electrical conductivity and mechanical properties were determined after incorporating acetylene black.

Development of conductive nitrile rubber and its blends with natural rubber, polyvinyl chloride and ethylene-propylene-diene rubber is described in chapter 4. Nitrile rubber was made conducting by the incorporation of acetylene black. The change in electrical conductivity and mechanical properties with the amount of acetylene black was studied. The conductivity and mechanical properties improved with the amount of acetylene black. Nitrile rubber was blended with NR, PVC, and EPDM and their electrical conductivity and mechanical properties were determined after incorporating acetylene black. NBR/NR blends were found to be more conducting than NBR alone, NBR/PVC and NBR/EPDM blends. NBR/NR blends of different compositions were prepared and their conductivity and mechanical properties were evaluated. The effect of temperature on the conductivity of different vulcanizates was also studied. The mechanical properties of conductive nitrile rubber were found to be better than those of silicone rubber loaded with the same amount of acetylene black. But the conductivity of silicone rubber is higher than that of NBR loaded with the same amount of acetylene black.

Preparation and characterization of a new conducting polymer, poly(p-phenylenediazomethine) is described in Chapter 5. This conjugated polymer based on glyoxal and p-phenylene diamine was prepared by the condensation reaction under different experimental conditions. The polymer formed was characterised by GPC, infrared spectra (IR), thermogravimetric analysis (TGA), and UV spectra. The effect of solvent and temperature on the polymerization reaction was studied by carrying out the reaction in different solvents such as N,N-Dimethylformamide (DMF), m-cresol, toluene and methanol. The d.c. conductivity of the samples prepared in DMF was found to be the highest. The molecular weight of the polymer prepared in m-cresol solvent is, Mn = 25660 and Mw = 69123.The polymer is thermally stable up to about 400^{0}C Thermal diffusivity of the polymer lies in between that of aluminium and iron, showing high thermal conductivity for the newly synthesized conducting polymer. The effect of dopants on the conductivity of the polymers was determined by doping the polymer with one molar solution of HCl, $HClO_4$ and I_2 in CCl_4. Perchloric acid was found to be a potential doping agent for the samples. The microwave conductivity and complex permittivity of the samples prepared in different solvents and doped with different doping agents was also determined.

To improve the processability of the novel conducting polymer prepared, blends of the polymer was prepared with polyethylene, poly(vinyl, chloride), and silica and their properties were evaluated. The details of such studies are presented in Chapter 6. The effect of addition of polyethylene, polyvinyl chloride and ultra fine silica to the conducting polymer was studied by the in-situ polymerization of glyoxal and p-phenylene diamine in different solvents, which contained different amounts of PE, PVC, and silica. The d.c. conductivity and microwave conductivity of each sample was measured. The effect of dopants like $HClO_4$, HCl and I_2 on the conductivity was also studied. The d.c. conductivity of the undoped polymer blends was decreased with increase in the amount of polyethylene, PVC, and silica. The d.c. conductivity of the blend was increased on doping with HCl, $HClO_4$ and iodine. The d.c. conductivity of all blends with polyethylene doped with HCl, $HClO_4$ and iodine was decreased with increase in the amount of polyethylene. The d.c. conductivity of the blends with PVC and silica doped with HCl and iodine was decreased with increase in the amount of PVC and silica, but it increased first, and then remained almost constant or slightly decreased on doping with $HClO_4$. Microwave conductivity, dielectric constant, and dielectric loss factor of the conducting polymer blends with silica and PVC were also determined at a frequency of 2.17 GHz. Effect of doping on the values of these dielectric properties were also studied

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1. K. G. Princy, Rani Joseph and C. Sudha Kartha, ***Studies on conductive silicone rubber compounds*****, Journal of applied polymer science, 69,** 1043-1050, (1998).
2. K. G. Princy, Rani Joseph and C. Sudha Kartha, ***Studies on conductivity of nitrile rubber and it's blends with NR, EPDM and PVC*** , Plastics Rubber and Composites. (Accepted for publication)
3. K. G. Princy, Rani Joseph, and C. Sudha Kartha, **Effect Of Temperature On Conductivity Of Nitrile Rubber Vulcanizates**, Plastics Rubber and Composites, (Communicated).
4. K. G. Princy, Rani Joseph, K. T. Mathew, Otto van Asselen, and C. Sudha Kartha, **Synthesis And Characterization Of A Novel Conducting Polymer-Poly (P-Phenylenediazomethine),** Synthetic Metals, (Communicated).
5. K. G. Princy, Rani Joseph, K. T. Mathew, Otto van Asselen, and C. Sudha Kartha, **Synthesis And Characterization Of Conducting Polymer Blends Of Poly (P-Phenylenediazomethine) With PE, PVC And Silica**, Synthetic Metals, (communicated).

List of Abbreviations

AB	Acetylene black
ASTM	American society for testing and materials
CCl_4	Carbon tetrachloride
cm	Centimetre
^0C	Degree Celsius
D.C.	Direct current
DBP	Dibutyl phthalate
DCP	Dicumyl peroxide
DMF	N,N-Dimethylformamide
DOP	Dioctyl phthaate
EMI	Electromagnetic interference
EPDM	Ethylene propylene diene rubber
G	Graphite
GHz	Giga hertz
gm	Gram
GPC	Gel permeation chromatography
HAF	High abrasion furnace
HCl	Hydrochloric acid
$HClO_4$	Perchloric acid
HDPE	High density polyethylene
I_2	Iodine
IPN	Interpenetrating polymer network

IR	Infrared
ISAF	Intermediate super abrasion furnace
LB	Lamp black
LDPE	Low density polyethylene
MBTS	Dibenzthiazyldisulphide
MgO	Magnesium oxide
min	Minutes
mL	Millilitre
ML(1+4)	Mooney viscosity determined using large rotor after a dwell time of one minute and rotor run of 4 minutes
mm	Millimetre
NBR	Nitrile rubber
nm	Nanometre
Nm	Newton metre
NR	Natural rubber
%	Percentage
PPD	p-phenylenediamine
PRI	Plasticity retention index
PVC	Poly (vinyl chloride)
rpm	Rotations per minute
S	Seimen
S	Sulphur
SA	Stearic acid
SBR	Styrene butadiene rubber
sec	Seconds

SR	Silicone rubber
TGA	Thermo gravimetric analysis
THF	Tetrahydrofuran
TMTD	Tetramethyl thiuram disulphide
UTM	Universal testing machine
V	Volts
ZnO	Zinc oxide
	Wavelength
ρ	Resistivity