PREPARATION AND SOLID STATE CHARACTERIZATION OF CONDUCTING POLYMER COLLOIDS

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SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF M.PHIL IN CHEMISTRY

DEPARTMENT OF CHEMISTRY

BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY

DHAKA-1000, BANGLADESH

AUGUST -1999

Bangladesh University of Engineering and Technology, Dhaka
Department of Chemistry

Certification of Thesis

A thesis on

"Preparation and Solid State Characterization of Conducting Polymer Colloids"

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has been accepted as satisfactory in partial fulfilment of the requirements for the degree of Master of Philosophy (M.Phil) in Chemistry and certify that the student has demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on August 14, 1999.

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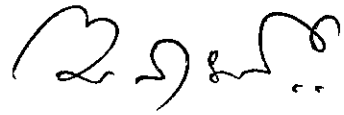

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ACKNOWLEDGEMENT

The author would like to express his sincere gratitude and thanks with pleasure to his respected supervisor, Dr. Al-Nakib Chowdhury, Assistant Professor, Department of Chemistry, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh, for his scholastic guidance and deep concern over this research work. His profound interest and valuable suggestions in this research work inspired the author to face problems with confidence.

The author is grateful to Prof. Dr. Enamul Huq, Head, Department of Chemistry, BUET, for his kind co-operation and inspiration during this research. The author wants to thanks to Prof. Dr. Md. Monimul Huque, Prof. Dr. Md. Manwarul Islam and Mr. Md. Nurul Islam, Assistant Professor, Department of Chemistry, BUET for their kindest supports and suggestions throughout the work. The author is also grateful to all other teachers and staff of Chemistry Department, BUET, Dhaka.

The author likes to express his gratitude and thanks to Dr. M. Qamrul Ehsan, Associate Professor, Department of Chemistry, University of Dhaka for his help, co-operation and valuable suggestion on this work. Special thanks are offered to Prof. Dr. Abu Jafar Mahmood and Prof. Dr. M. Abul Quyser, Department of Chemistry, University of Dhaka for their co-operation on this work.

The author wants to thank Dr. Md. Aminur Rahman, SSO, and Mr. Md. Junab Ali, PSO, IGCRT, BCSIR, Dhaka for their help in this research work. The author also thanks to Mr. Ruhul Amin Khan Ex M. Phil. Student and Mr. M. Abu Yousuf M.Phil. students, for their kind helps. Sincerely acknowledged to Mr. Faruque-Uz-Zaman Chowdhury and A.T.M. Kawsar Jamil Ph.D. student, Physics Department, BUET for their helps. Special thanks to Mrs. Nurtaj Begum for her help in this work.

The author is highly grateful to the BUET authority for the financial support of the work. The author likes to thank Mrs. Rumana Begum for her inspiration in this research work. The author also wants to thank Mr. Md. Liaquat Ali for his help in computer composing of the thesis.

Finally, the author extends his whole hearted thanks to his relatives, friends specially Mr. Momin, Mr. Md. Nazrul Islam and Mrs. Nahid Sultana for their inspiration and valuable comments to his research work.

J.M. Arifur Rahman 14.08.1999

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Abstract

Preparation and characterization of colloidal dispersions of conducting polymer-inorganic oxide composites have been described. Aniline, o-toluidine and 2-chloroaniline were polymerized chemically in the presence of fine colloidal silica particles in aqueous media and given a sufficient silica concentration, colloidally stable poly(aniline)/silica, poly(o-toluidine)/silica and poly(2-chloroaniline)/silica composite were obtained. These composites have been characterized by a wide range of experimental techniques including optical microscopy, optical spectroscopy, sedimentometry for particle size surface area measurement, x-ray diffraction and d.c. solid-state conductivity measurements. Adsorption of methyline blue aqueous solution onto PANI/silica have also been studied. Electrochemical synthesis of PANI/silica has been evidenced based on the elemental analysis, density and infrared spectroscopic measurements. Electrochemical degradation of PANI/silica on overoxidation and repeated potential sweeping has also been investigated.

Elemental analysis for the silica content indicated that chemically synthesized composite matrix contains as high as 40% silica in the matrix. On the other hand, electrochemical measurements for the bulk polymer sample and the polymer/silica samples clearly indicate different values for each. The particle size distribution of the composites seems to be ranging from 50 - 1 μm. A wide distribution of white images in the micrographs of polymer/silica samples may indicate the presence of silica particles in the composite matrix.

IR spectroscopy studies yielded useful, qualitative information on the polymer/silica composites synthesized chemically and electrochemically. From the spectra, the band characteristics of aniline, o-toluidine and 2-chloroaniline confirmed the presence of these monomer rings in the respective polymer. The IR spectra observed for the studied samples exhibited absorption bands attributable to both polymer and silica components.

UV-VIS spectra of the studied polymer/silica samples resemble to those of the bulk polymers. The strong absorption maxima observed in the ultraviolet region may be attributed to with interband transition and the other intense band in the visible region probably results from interaction between the polymer and the dopant anion. The present optical data provides elucidation of the band structure of poly(aniline)/silica and a band gap of 4.32 eV for this system was obtained from the data.

The electrical conductivity of the polymer/silica composite has been found to be lowered by a few order of magnitude relative to the corresponding bulk polymer. However, their conductivity values still fall in the range of conductivities for semiconductors. The diffuse x-ray scattering pattern of the polymer/silica composites indicate the amorphous nature of the materials. The scattering pattern of the bulk polymer and that of polymer/silica seem to be indifferent. This finding suggests that incorporation of silica particles do not have any influence on the structure of the composites.

Surface area measurements show that poly(aniline)/silica composites have much higher area than that of its bulk polymer. The incorporation of fine silica particles to the polymer might lead to this increased surface area. Adsorption of methylene blue solution on to the poly(aniline)/silica matrix has been found to occur.

Electrochemically synthesized poly(aniline)/silica electrode was found to be as electroactive as the bulk conducting polymer. The stability and durability of the poly(aniline)/silica electrode in repeated oxidation/reduction cycles and its degradation at highly positive potentials were examined. The results obtained from cyclic voltammograms indicate that although overoxidation takes place with poly(aniline)/silica electrode, the extent of degradation is not as drastic as with bulk poly(aniline) suggesting a better electrochemical stability of the composite electrode relative to the bulk polymer electrode.

CHAPTER 1

INTRODUCTION

1.1 New materials

We live in a world of man-made materials. Steel, aluminium, plastics, ceramics, copper, glass, paints and all the others are the concrete substance of our ideas, our designs, our product plans and blueprints. Materials have always been vital to human civilization. But now in the twentieth century materials not just one, but many have become the most important single factor on which the advance of technology and industry depends. Despite the amazing variety of modern day materials, the search still goes on for better materials to meet new and critical service requirements not only in an advance technology area such as aerospace, but in the manufacture of industrial and consumer products as well. Also, better materials are needed to meet higher quality and reliability standards, epitomized by long term product warranties and the demand for safer products. Finally, the search goes on constantly for new and better materials to lower costs. Industries develope or select materials with the right combination of properties to meet performance and economic requirements, and they are unconcerned whether the chosen materials is a metal, a plastics, a green cheese or a composite. Most industrial materials, specially solids, are used in building products and structures, and some are mainly used in the building and construction field. Compare to the other two states of matter, solids have useful mechanical properties such as strength, hardness, and rigidity. At the microlevel, solids are characterized by a greater regularity of structure than gases and liquids. Crystalline materials, such as metals and ceramics, represent the true microstructure of the solid state, where molecules are arranged in regular and repeatable patterns. The microstructure of polymers like plastics, although more amorphous than that of metals, is made up of molecular chains composed of regular repetitive units. Moreover, now a days, the wide variety of choices of combination of materials rather than a single

compounds, giving rise to new combination of properties are used. As for example a highly electrically conducting plastic by combination of copper in the right form (4% by volume) with poly (vinyl chloride) composite are used [1].

Composites are best known for their mechanical properties. The stiffest and the strongest materials known or believed to be possible, consist of the elements and binary compounds of the covalently bound solids: graphite, diamond, boron, silicone carbide, alumina etc. They are unique group of elements and compounds which contains the highest density of strongest interatomic bonds and these strong bond coupled with deep interatomic potential wells, implying large sublimation energies, make these materials the stiffest known. Polymers reinforced by fine fibers having high strength and/or stiffness are frequently referred to as advanced composites. The most commonly used fibers are glass, carbon and kevlar (an aramid) having a diameter of about 10μm. Typical matrices are polyester and epoxy resins and, more recently, high temperature thermoplastics. Normally such materials are used to form laminated plate like constructions, where the thickness is very much less than the length and width. Aromatic polymer composites are a new class of advanced structural material based on carbon fibre where the polymer matrix is a tough thermoplastic rather than a conventional thermostate. Metal matrix composites (MMC) are being developed because it has advantages over thermosetting resins. Polymer matrix composites (PMC) are also developed for its very good structural, electrical and other physico-chemical properties. The important linear polymers are all based on carbon and are designed at a molecular level to control the average length of the chain, the strength of the forces between the chains, the stiffness of the individual chain and the regularity with which the chains are packed together. Because of the covalent bonding polymers are

semiconductors. Extensive doping with oxidizing or reducing is done for conduction. Thus the PMC shows a better mechanical and electrical properties.

1.2 Types of materials

Materials can be classified in different ways depending on their use, structure, origin and property. These can be classified mainly into five types.

(A) Metals

Metals are crystalline solid materials consist of metal atoms distributed in a definite pattern resulting from their close packing. The types of close packing arrangement depends upon the size and electronic configuration of the atoms involved in the formation of crystal lattice. Since the metal atoms are all in direct contact with one another in the lattice and their valence electrons are in identical energy states, it is believed that the electrons are free to migrate between atoms. Metals atom has an excess of low energy orbital vacancies. These vacancies enable valence electrons to move from near a certain nucleus to near any other nucleus where their position remains indistinguishable from the first. Thus metals may be pictured as a collection of positive atomic cores embedded in a fluid of electrons or sea of electrons. For this fluid of electrons, metals are good conductors of electricity and heat. Metals have metallic lustre; they are malleable, ductile and high melting points.

Metals have simple crystal lattices since metallic bonding envisages closest packing of atoms- one layer above another. Metals may have any system of seven common crystal system. Fe, Cu, Al, Ag, Au etc are the most common metals which are very useful to us.

(B) Semiconductors

Semiconductors are special kind of materials which have the properties of semiconductivity. Semiconductivity is an electrical property of materials. A relatively small group of elements and compounds has an important electrical property, semiconduction in which they are neither good electrical conductors nor good electrical insulators. Instead, their ability to conduct electricity is intermediate. Si, Ge, impure ZnO, impure NiO are some examples of semiconductors.

The magnitude of conductivity in the simple semiconductors falls within the range 10^{-6} to 10^{-1} Ω^{-1} cm^{-1}. This intermediate range corresponds to band gaps of less the 2eV. Both conduction electrons and electron holes are charge carriers in a simple semiconductor.

In a semiconductor element, the energies of the valence electrons which bind the crystal together lie in the highest filled energy band, called the valence band. The empty band above, called the conduction band, is separated from the valence band by an energy gap. The magnitude of the energy gap or the width of the forbidden energy zone, is characteristic of the lattice alone and varies widely for different crystals.

The transfer of an electron from the valence band to the conduction band requires high excitation energy to overcome the potential barrier of the forbidden energy zone. Consequently, such elements behave like an insulator at low temperatures. The application of heat or light energy may give enough energy to some electrons in the valence band to the excite them across the forbidden zone into the

conduction band. These electrons in the conduction band are now free to move and can carry electricity (Fig. 1.2.1).

Semiconductors are of two kinds such as

(i) Intrinsic semiconductor

(ii) Extrinsic semiconductor

(i) Intrinsic semiconductors : If a pure, elemental substance shows the semiconducting properties, it is called intrinsic semiconductor. Pure Si, Ge shows these semiconducting properties. For this semiconduction results from the thermal promotion of electrons from a filled valence band to an empty conduction band. There, the electrons are negative charge carriers. The removal of electrons from the valence band produces electron holes which are positive charge carier and identical to the conduction electrons (Fig. 1.2.1(a)). This overall conduction scheme is possible because of the relatively small energy band gap between the valence and conduction bands in silicon. If δ is the conductivity of semiconductor then for intrinsic semiconductor, we can write

$$\delta = nq(\mu_e + \mu_n) \qquad 1.2.1$$

where

$n \rightarrow$ density of conduction electron

$q \rightarrow$ charge of single carrier

$\mu_e \rightarrow$ carrier mobility of electron

$\mu_n \rightarrow$ carrier mobility of hole

(ii) Extrinsic semiconductors: Extrinsic semiconduction result from impurity additions known as dopants, and the process of adding these components is called doping. These types of semiconductors are Extrinsic semiconductors. At room temperature the conductivity of semiconductors results from electrons and holes

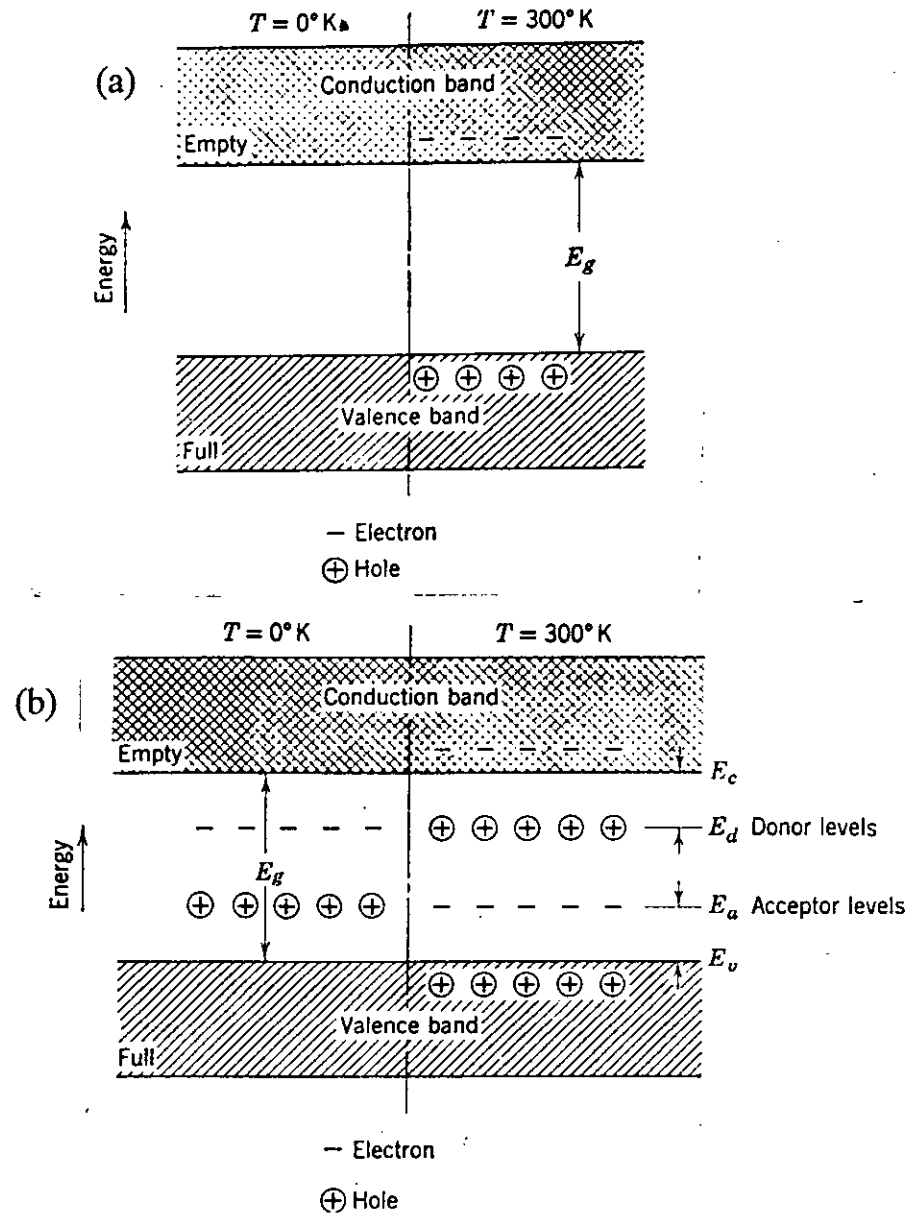


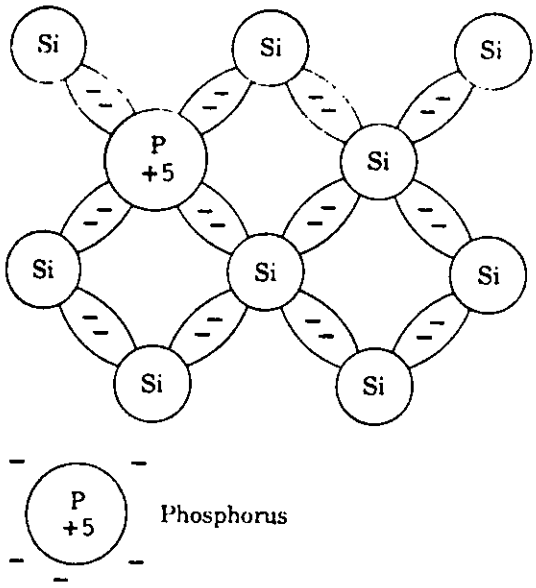
Fig. 1.2.1: A pictorial representation of an (a) intrinsic and (b) extrinsic semiconductor

introduced by impurities in the crystal. The presence of an impurity lowers considerably the activation energy necessary to transfer an electron from the valence band to the conduction band. This indicates that the ground state energies of such easily excited electrons must lie in the forbidden energy region. Two such discreate energy levels, known as donor levels and acceptor levels, may be introduced into the forbidden energy zone at a small interval of energy below the conduction band or above the valence band (Fig. 1.2.1(b)). Donor levels give rise to electrons in the conduction band, whereas acceptor levels lead to the formation of holes in the valence band. Impurity of Si, with B, P; NiO, ZnO, are the examples of extrinsic semiconductors. Extrinsic semiconductors are of two kinds such as p-type extrinsic semiconductor and n-type extrinsic semiconductor

p-type extrinsic semiconductors : The p type semiconductor is obtained when the impurity atoms have fewer valence electrons than the silicon or germanium atoms of the original crystal. When a trivalent element such as B, Al, Ga, In is substituted for Si atom, the structure will be locally incomplete and the impurity atom will acquire an extra electron from a nearly bond in the lattic to approximate the tetrahedral cloud distribution of the lattice. This creates a positive hole localized near the impurity, which will attempt to neutralize itself by taking an electron from another neighboring bond. Then again a hole is formed in place of this electron and it will neutralize itself by taking another electron from the next neighboring bond. Such way the positive holes carry electricity in the extrinsic semiconductor. So it is called p(i.e. positive) type semiconductor (Fig. 1.2.2(b)) Cu_2O also p-type semiconductor.

n-type semiconductors : The n-type semiconductor arises from substitution of impurity atoms having more valence electrons than Si or Ge atoms. Elements such

(a)



(b)

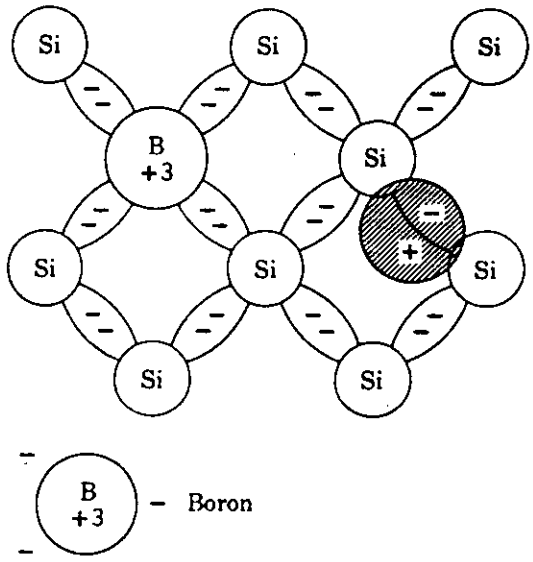


Fig. 1.2.2: Types of impurity semiconductors (a) n-type (b) p-type

as P, As, Sb, and Bi have five valence electrons. When such an element is substituted for a silicon atom, four of its five electrons will enter the inter-atomic bonds, but the fifth electron will be only slightly attracted by the excess of the positive charge on the nucleus. Thermal agitation even at room temperature is sufficient to transfer this electron to the conduction band. Since conductivity is due to the motion of electrons in the conduction band, this semiconductor is called n-type and the impurity is called the donor (Fig. 1.2.2(a)).

(C) Ceramics

Ceramics are crystalline compounds of metallic and non metallic elements. The ceramic family is large and varied, including such materials as refractories, glass, brick, cement and plaster, abrasives, sanitaryware, dinnerware, porcelain enamel, ferroelectrics, ferrites and dielectric insulators.

Ceramics are crystalline materials, like metals, but because of fewer free electorons, they have little of essentially no electrical conductivity at room temperature. They have high stability and on average, have higher melting points and greater chemical resistance than metals and organic meterials. They are generally the hardest of the engineering materials. They are extremely stiff and rigid. Under mechanical stress, they have little or no yield and exhibit brittle fracture. A broad range of metallic and nonmetallic elements are the primary ingredients in ceramic materials.Some of the common metals are Al, Si, Mg, Be, Ti, and B Non metallic elements with which they are combined are oxygen, C or N. Ceramics can be either simple, one phase materials composed of one compound, or multiphase, consisting of a combination of two or more compounds are single oxides such as alumina (Al_2O_3) and magnesia (MgO), and mixed oxides such as cordierite (magnesia alumina silica) and forsterite (magnesia silica).

Ceramics are structurally quite complex. Because ceramic crystalline phases are compounds, the unit cells often contain three or four different atoms. Also, there are relatively few free electrons in ceramic structures, as compound to metals. Instead, electrons of adjacent atoms are either shared to produce covalent bonds or treansferred from one atom to another to produce ionic bonds. These strong bonding mechanisms are what account for many of ceramic's properties, such as high hardness, stiffness and good high temperature and chemical resistance.

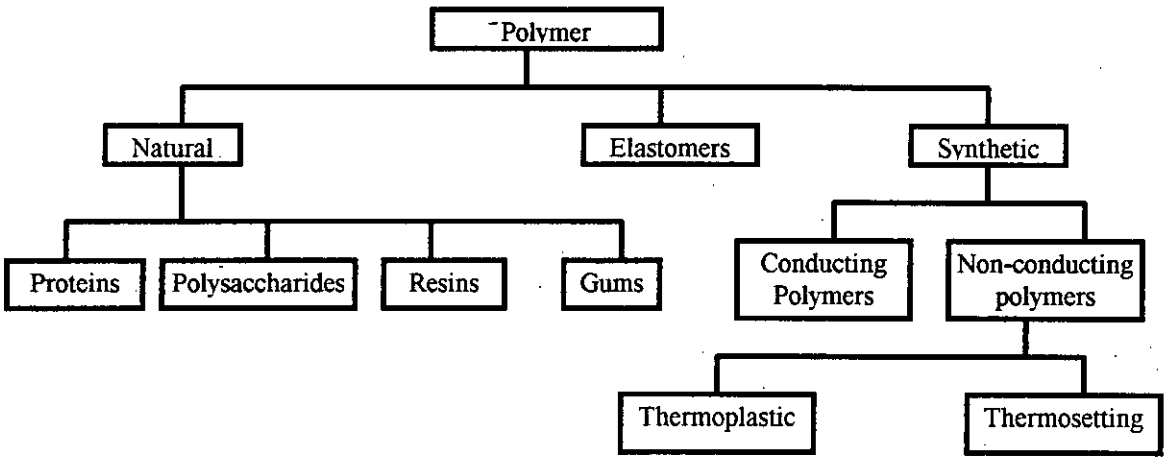
A basic steps in producing ceramic products are (i) preparing the ingredients for forming (ii) shaping or forming the part (iii) drying and (iv) firing or sintering. The drying step depends on the type of ceramic and application, and is sometimes not required. The raw materials are usually in the form of particles or powder. In the preparation step, the ingredients are weighed, mixed, and blended either wet or dry. In dry processing, the mixture is sometimes heated in order to cause preliminary chemical reactions. In wet processing, the required plasticity for shaping is obtained by grinding and blending plastic clays with finely pulverized nonplastic ingredients and adding alkalies, acids, and salts.

(D) Polymers

Polymers are giant molecules composed of hundreds or thousands of the basic structural unit which is composed of a limited number of atoms strongly bonded together. This basic unit is called monomer. Polymers are chain like and macromolecules. The repeat unit (or basic unit) of the polymer is usually equivalent or nearly equivalent to the monomer. In some cases the repetition is linear, much as a chain is built up from its link. In other cases the chains are

branched or interconnected to form three dimensional networks. The length of the polymer chain is specified by the number of repeat units in the chain. This is called the degree of polymerization. Starch, protein, lignin, cellulose, silk etc. are natural polymers and poly(aniline) (PANI), poly(pyrole) (PP), poly(aniline)/SiO_2 (PANI/silica) polyethylene, nylone, synthetic rubber, polypropylene etc. are the example of synthetic polymers. Some polymers are conductor of electricity although most of the polymers are non-conductor or insulator.

Polymers can be classified in different ways depending on their use, structure, origin and property. Depending on the nature of the polymers a broad clsssification is diagramically shown below:



(i) Natural polymers:

Natural polymers usually have more complex structure. They are classified as (a) Proteins (b) Polysaccharides (c) Resins (d) Gums.

(a) ***Proteins:*** Proteins are essential for life. All characteristics commonly attributed to living things such as reproduction, growth, movement, metabolism

and sensory perception, are entirely dependent on the function of proteins. Proteins are synthesized biologically as linear polymers of twenty amino acids.

(b) ***Polysaccharides:*** Polysaccharides are carbohydrate polymer in which monosacchride (glucose, fructose etc) residues are linked directly through glycosidic linkages. They are found in animal, plant, and microbial kingdoms, where they may serve for energy storage, as structural materials.

(c) ***Resins:*** A natural resin is any of various solid or semi-solid amorphous, fusible, flammable natural organic substances that are usually transparent or translucent and yellowish to brown, are formed especially in plant fecretions, are electrical non-conductor and are used chiefly in medicine, varnishes, printing inks, plastics and sizes.

(d) ***Gums:*** Gums are very complex, amorphous substances of a polysacharide nature. They contains very small amounts of Ca, Mg, K with the composition of C, H and oxygen. They are used in pharmacy and industry.

(ii) Elastomers

Elastomers can either be natural or man made. Like fibres, elastomers are considered apart from other polymeric materials because of their special properties. Unlike fibers, elastomers do not in general lend themselves to uses. Elastomers must be amorphous when unstretched.

(iii) Synthetic polymers

Synthetic polymers are man made. They are synthesized in the laboratory by applying heat, pressure or catalysts (initiators). They are of two kinds such as (a) Conducting polymers and (b) Non-conducting or Insulator polymer.

(a)Conducting polymers: During the last two decades, a new class of organic polymers are synthesized which conduct electrical current. These polymers are called conducting polymers [2]. In general polymers are insulating materials having conductivities ranging from 10^{-10} Scm^{-1} for poly (vinyl chloride) to $10^{-18}Scm^{-1}$ for poly (tetrafluoro-ethylene), which are many orders of magnitude below compare to the conductivities associated with metals ($>10^{6}Scm^{-1}$). As a result polymers have found wide spread acceptance in a myriad of insulating and structural applications through out the electronic industry. One of the earliest approaches to make polymers conducting is to prepare a composite of polymers and a conductive filler, such as metal powder, graphite powder, flake or wire etc. Conductive fillers remain embedded more or less evenly dispersed in the polymer materix and conduct electric current. But these composites can not be regraded as conducting polymers because the polymers present in such composites are non-conducting [3-6]. When anions like Cl^-, ClO_4^-, BF_4^- etc. are doped chemically to organic polymers, their electrical conductivity increases. Again when silicon dioxide is dopped in to these polymers, their stability is increased although its electrical

conductivituy may be decreased. Poly(aniline), PANI, PANI/silica which are prepared in an acidic (HCl) solution are these type of polymers.

(ii) Non-conducting polymers

The polymers which can not carry electricity are non-conducting polymers or insulating polymers. They are of two kinds such as (a) Thermoplastic (b) Thermosetting.

(a) ***Thermoplastic:*** A thermoplastic polymer is one that is capable of being repeatedly softened by heating and hardening by cooling through a characteristic temperature range, and that in the softened state can be shaped by flow into articles by molding or extrusion. Thermoplastic applies to those materials whose change upon heating is substantially physical.

(b) ***Thermosetting:*** A thermosetting polymer is one that is capable of being changed into a substantially infusible or insoluble prolduct when cured by heat or other means. The cured polymer may be termed thermoset.

E. Composites

Since 1965 has a distinct discipline and technology of composite materials begun to emerge. That is 80% of all research and development on composites has been done since 1965 when the Air Force launched its-all out development program to make high performance fiber composites a practical reality. There are two major reasons for the revived interest in composite materials. One is that the increasing demands for higher performance in many product areas specially in the aerospace, nuclear energy and aircraft fields is taxing to the limit our conventional monolithic

materials. The second reason the most important for the long run is that the composites concept provides scientists and engineers with a premising approach to designing, rather than selecting, materials to meet the specific requirements of an application.

The term "composite" refers to something made up of various parts or elements. In definition of composite depends on the structural level of the composite we are thinking about. At the submicroscopic level that of simple molecules and crystal cells all materials composed of two or more different atoms or elements would be regarded as composites. This would include compounds, alloys plastics and ceramics. Only the pure elements would be excluded. At the microscopic level (or microstructural level) that of crystals, polymers, and phases a composite would be a material composed of two or more different crystals, molecular structures, or phases. By this difinition most of our traditional materials which have always been considered monolithic would be classified as composites. At the macrostructural level which is most useful for composites, the difinition of composites is that they are a mixture of macroconstituent phase composed of materials which are in a divided state and which generally differ in form and/or chemical composition. Note that, contrary to a widely held assumption, this difinition does not require that a composite be composed of chemically different materials, although this usually the case. The more important distinguishing characteristics of a composite are its geometrical features and the fact that its performance is the collective behaviour of the constituents of which it is composed. A composite material can vary in composition, structure, and properties from one point to the next inside the material.

The major constituents used in structuring composites are fibers, particles, laminas, flakes, filters, and matrixs. The matrix which can be thought of as the body constituent gives the composite its bulk form. The other four, which can be referred to as structural constituents determine the character of the composites internal structure. An special type of composite, fiber glass embedded in a polymer matrix is a relatively recent invention but has in a few decades, become a commonplace material. Characteristic of good composites, fiber glass, provides the "best of both worlds", it carries along the superior properties of each component, producing a product that is superior to either of the components separately. The high strength of the small diameter glass fibers is combined with the ductility of the polymer matrix to produce a strong material capable of with standing the normal loading required of a structural material.

1.3 Application of new materials

Metals, Semiconductors, Ceramics, Polymers and Composites are the new materials. The new materials which have achieved prominence on the engineering scene in the last ten years or so or which are confidently expected to do so, are reviewed under the headings: composites, ceramics (inorganics), surface engineering, polymers and new metals. Compositing is shown to be a unifying influence in designing new materials for specific functions. Composites are used as starting materials for many compounds, for instance, a highly electrically conducting plastic by combing copper in the right form (only 4 vol% is needed) with polyvinylchloride. The wings of the AV8B (harrier) aircraft are made of graphite fibre in a woven form in an epoxy resin. It is moulded to shape in an autoclave. A set of parallel fibres in a matrix is a very anisotropic solid which can be used to very good effect in certain devices in computer. Metal matrix

composites are being developed because the metal as a matrix say Al or Mg for low temperature aerospace applications, or Ti for the high temperatures, has advantages over thermosetting resings. The principle of compositing materials is also used in a very sophisticated way in what is called band gap engineering in microelectronics. This has been driven by the need to create complex heterjunction lasers. New metals are used as solvent for other elements because they dissolve other elements more readily in the liquid than in the solid state. Because of the covalent bonding polymers are semiconductors and the intrinsic conductors known to be unstable in air, extensive doping with oxidizing or reducing agents is necessary to produce conduction [7]. One of the most important applications of conductive polymers is as electrodes in the rechargeable batteries. In such applications, use is made for the electrochemical reversibility of the polymers acting as electrodes [8]. The use of thermoplastic, linear chain, polymers as the matrix phase promises to satisfy the criteria which we have defined as necessary for advanced structural composites to become major general engineering materials [9]. The semiconductor is used in the transistors. The normal polymers are used as insulator both for heat and electricity.

1.4 Colloidal state of the materials

Colloids or colloidal substances can be arbitrarily defined as matter in a fine state of subdivision, larger than atomic and simple molecular dimensions but smaller than particles visible to the naked eye. This definition covers all matter in a disperse state having a particle size from 1 mμ to 1μ. Dispersions with a particle size larger than 1μ are called coarse suspensions or dispersions; those having particles smaller than 1mμ are termed molecular dispersions or true solutions. The

phase formed by disperse particles is called the disperse or internal phase, and the medium in which the particles are suspended is called the dispersing or external or continuous phase.

Colloids cover innumerable materials, nearly all the materials of ordinary life such as fine suspensions of inorganic compounds and molar soaps, proteins, organic high polymers, and many others. Any rigid classification of colloidal systems is extremely difficult and remains incomplete, because a considerable overlapping of properties occurs among various colloidal substances. Since both the disperse and dispersing phases may be liquid, solid, or gas a number of possible disperse systems can be obtained as (i) solid in liquid, (ii) liquid in liquid, (iii) gas in liquid, (iv) solid in solid, (v) liquid in solid, (vi) gas in solid (vii) solid in gas and (viii) liquid in gas. Colloidal suspensions as exhibited by most colloidal systems are solid in liquid. Again, colloidal systems with liquid as an external phase are considered under two main groups, lyophobic (liquid hating) and lyophilic (liquid loving) colloids. When water is a dispersing medium, the terms hydrophobic and hydrophilic are used respectively. Lyophobic or hydrophobic colloids are dispersions of the particles composed of a large number of atoms or molecules which are of sufficient size (0.01 to 1μ) and refractivity to be visible in the ordinary ultramicroscope. Lyophobic colloids are mostly inorganic compounds such as metal particles and certain hydroxides. Lyophilic colloids are usually macromolecular dispersions of organic high polymer, protein, and soaps. Such dispersions are not visible in ultra microscope because of their smaller size (0.001μ to 0.01μ). Many colloidal systems exhibit the properties between lyophobic and lyophilic colloids to a varying degree. Such colloidal dispersions as hydrous silica, stannic oxide, and some sulfur sols are classed as lyophobic colloids in their behaviour resemble lyophilic systems. Precipitation, when it does

occur, is often reversible, and the solid can be redispersed when the electrolyte is washed away.

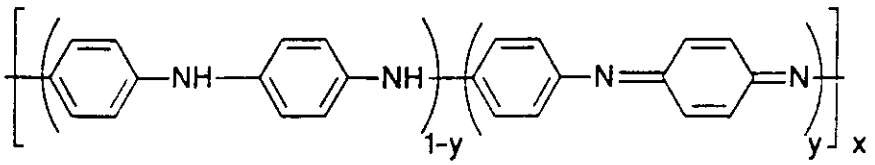
Colloidal particles dispersed in a liquid exhibit an oscillatory or zigzag motion known as the Brownian movement. This phenomenon is the result of the bombardment of the particles by the liquid molecules which are in a state of thermal motion of either transitory or vibrational character. Although the oscillating particles acquire the same average kinetic energy as the liquid molecules, their velocity is much less because of their relatively large mass as compared to the molecules of liquid. The Brownian movement tends to keep the colloidal particles is suspension against gravitational forces, but at the same time it results in very frequent, mutual collisions between the particles. These collisions would cause the particles to adhere and finally precipitate, if there were no repulsive force between them. These repulsive forces have their origin in the electric charge carried by colloidal particles, and stabilized the colloids [10]

1.5 Poly(aniline)

PANI, whose structure was first described by English and German chemists at the turn of the century, consists of up to 1000 or more repeating units. It exists in several oxidation states with electrical conductivities varying progressively from 10^{-11}S per cm to more than 10 S per cm. Different compositions of PANI have different colours and electrical properties. It is synthesized easily by electrochemical or chemical oxidation of aniline in aqueous acidic media using common oxidants, such as ammonium peroxy disulfate. Mechanically flexible, dark-blue films of conductive PANI also have been achieved by protonic doping of emeraldine films cast from N-Methylpyrrolidinone solutions. Protonic doping

accomplished by dipping the emeraldine films in acid or passing a gaseous acid over them, protonates the imine nitrogen atoms in the back bone of the polymer.

Generalized formula for polyanilines



Various PANI can be defined by varying y in the generalized formula for the polymer. However, the myriad values y can take make the redox chemistry of the system very complex, particularly in aqueous media, where concurrent redox and protonation deprotonation processes occur. Here x is a positive integer.

Before 1980, little research had been done on PANI. However, Marcel Jozefowicz and coworkers at the centre National de la Recherche Scientifique in Paris found in 1968 that the conductivity of PANI increases by orders of magnitude as the pH of the acid it is doped with declines. They also recognized that PANI could serve as an electrode material for reversible batteries. PANI are generally amorphous, but many are in partially crystalline forms. A highly conducting state of PANI is accomplished by simple protonation of the imine nitrogen atoms in the emeraldine base backbone. Because protonic doping does not change the number of electrons in the polymers, its conductivity depends on the pH of the solution it is treated with [11]. By mixing aniline and colloidal silica, we can make synthesis of PANI/silica composites. Again from the derivatives of aniline such as O-toluidine,

2-chloro-aniline, we can prepare poly(o-toluidine)silica (CH_3- PANI/silica) and poly(2-chloro-aniline)/silica (Cl- PANI/silica) composites.

1.6 Silicon dioxide

The most important ceramic compound is silica or silicon dioxide (SiO_2). Widely available in raw materials in the earth's crust, this material by itself and in chemical combination with other ceramic oxides (forming silicates) represents a large fraction of the ceramic materials available to engineers. For this reason, the structure of SiO_2 is important. In fact, there is not a single structure to describe, but many (under different conditions of temperature and pressure). For a representative example, Fig. 1.6.1 shows the cristobalite (SiO_2) structure. There are 24 ions (eight Si^{4+} and 16 O^{-2}) per unit cell. In spite of the large unit cell needed to describe this structure, it is perhaps the simplest of the various crystallographic forms SiO_2. The general feature of all SiO_2 structure is the same a continuous connected network of SiO_4^{4-} tetrahedra. Although the basic SiO_4^{4-} tetrahedra are present in all SiO_2 crystal structures, the arrangement of connected tetrahedra changes [12]. The equilibrium structures of SiO_2 from room temperature to its melting point are summarized in Fig. 1.6.2.

Silicon dioxide is an acidic oxide. It is very inert. General silica is a freshly powder but colloidal silica which is called ludox is semi-liquid. Silica is surface active substance. It has high surface area. A Feng *et al.* studied on water adsorption and desorption kinetics on SiO_2 insulation [13]. They studied it by thermo-gravimetrically, FTIR spectrometrically. J Laszlo *et al.* studied monosized SiO_2 base micro spheres for chromatographic separations [14].

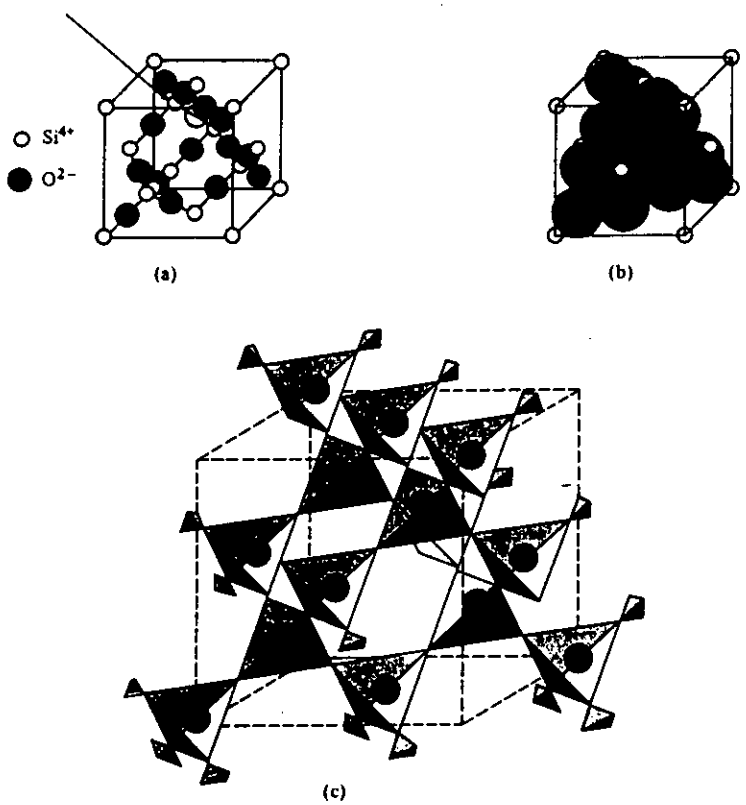


Fig. 1.6.1: Unit cell of SiO_2 : (a) ion position (b) full size ions and (c) the connectivity of SiO_4^{-4} tetrahedra.

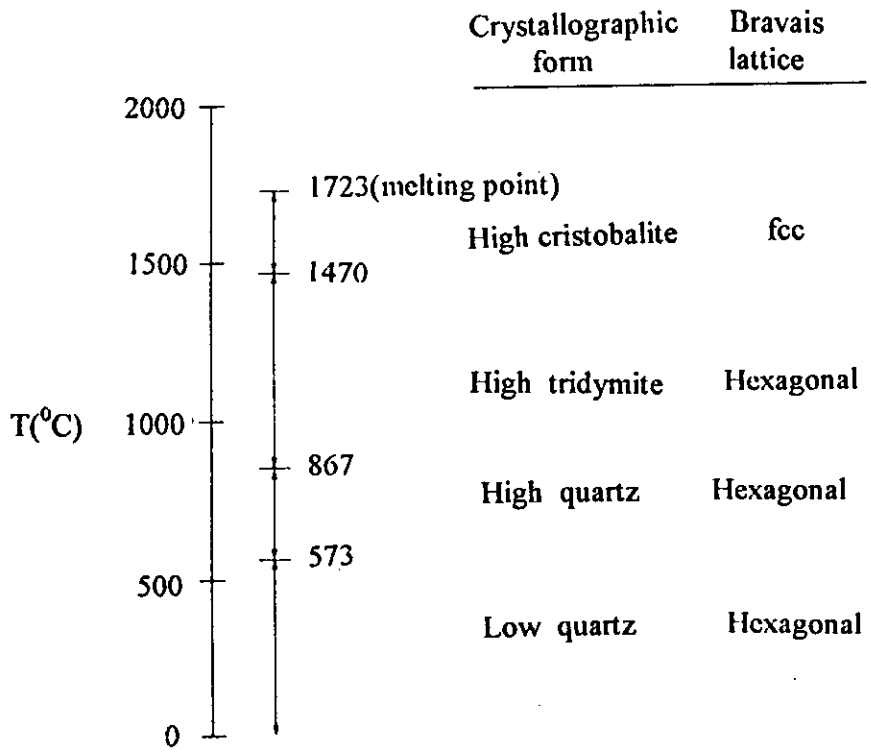


Fig. 1.6.2 : Different forms of SiO_2

Again silica can be used as catalyst for ammoniam decomposition and can be used as catalyst for the manufacturing of olefin polymers containing transition metal compounds and ionic compounds. Again it can be used eatalyst for catalytic cracking of polystyrene. Recently silica is used for preparation of colloidal nanocomposites with PANI, PP etc.

1.7 Review of literature

Many researches was carried out on composite materials. A. R. Bunsell has described the fibres for metallic and ceramic composites [15]. T. S. Raman *et al.* has carried out a research on advanced fibre reinforced composites. They used many techniques such as Dielectrometry, FT-IR spectoscopy, Ion graphing and Luminescence [16]. The development of composite materials can help to prepare high temperature materials. R Metselaar *et al.* have developed the composite materials which can serve a number of purposes such as to protect the electrodes from the corrosive combustion atmosphere at temperature upto 1450°C [17]. In 1964, W.A. little synthesized a superconductor at room temperature with backbone and large polarizable side groups which led the discovery of new organic compounds with high electrical conductivity [18]. In the early 1980 exitement ran high when several prototype devices based on conductive polymers, such as rechargeable batteries and current rectifying p-n junctin diodes [19] were announced. Among the many polymers known to be conductive, PANI, poly(acetylene), PP and poly(thiophene), have been studied most intensively [20-26]. A dependence of the electrical strength on thickness, area and volume of dielectric is demonstrated for poly (propylene) film by S. Cygan and J. R. Laghari

[27]. It was found that the electric strength of polymer film decreases with volume. It was shown that the function of electric strength is not simply dependent on the volume as obtained from theory of extreme values but that an increase of the volume by increasing the thickness of the dielectric is much more significant than same increase of the dielectric volume caused by an increase in area.

D.K. Das Gupta *et al.* synthesized polymer ceramic composites by introducing the ceramic particles into the polymer matrix [28]. They explained the electrical and dielectric properties of this composite.

M. Davies *et al.* explained the polyethersulphone and its fracture behaviour polyethersulphone has properties similar to many traditional engineering thermoplastics at room temperature. However, the degradation of these properties with increasing temperature is considerably more gradual [29].

Poly (dimethylsilozane)/SiO_2 and SiO_2/ TiO_2 composites have been successfully prepared using a sol-gel process by J. Wen and J.E.Mark [30]. The hydrolysis and sol-gel transition reaction of the poly(dimethyl siloxane)/SiO_2 system have been studied by nuclear magnetic resonance, gel permeation chromatography, solvent extraction and shear modulus tests.

PANI/Poly(propylene) composites were prepared by oxidative polymerization of aniline in biaxially stretched poly(propylene) microporous films with ammonium peroxydisulfate as the oxidant by C. Zhao *et al.* [31]. A continuous permeation diffusion polymerization process was used in order to incorporate more PANI in the composite.

Planes, Jerome *et al.* prepared PANI and determined the A.C. conducting properties of conducting polymers blends based on PANI [32]. S. A. Mallick *et al.* bioleached Cu from chalcopyrite ores coated with PANI film [33]. C. G. Innocenzo *et al.* used Cu dispersed into PANI films as an amperometric sensor in alkaline solution of amino acids and polyhydric compounds [34].

In 1979, Diaz *et al.* produced the first flexible, stable PANI film with high conductivity (100 Scm^{-1}). The substance was polymerized on a Pt-electrode by anodic oxidation in acetonitrile [35].

In reeent years, considerable research has been devoted to the development of novel processable forms of relatively air stable conducting polymers such as PP and PANI [36]. One approach is the preparation of colloidal dispersions of such materials. Most workers have focused in dispersion polymerization techniques as the preferred method of synthesizing conducting polymers colloids. For example, Toki *et al.* have described the preparation of poly(vinyl pyrrolidone)/silica hybrids via sol-gel chemistry [37]. S. Maeda, R. Corradi, and S. P. Armes have described the synthesis and characterization PP/silica microparticles [38]. Wung *et al.* have reported the preparation and characterization of poly(phenylene-vinylene)/silica composites [39]. Kramer *et al.* have synthesized PANI glasses by the in situ chemical polymerization of aniline [40].

More recently, Armes *et al.* reported the synthesis of colloidal nano composites of conducting polymer using small inorganic oxide particles as a particulate dispersant. They studied on PANI/silica, PP/silica nanocomposites. They studied adsorption of DNA on this nanocomposites [41-45]. J. Jinsoo measured the

microwave dielectric constant of PANI and studied its application to EMI Shielding [46]. R. B. Daniel *et al.* studied the polymer electroluminescent devices with PANI electrodes [47]. X. H. Quan *et al.* studied the "Electrically conductive PANI/Poly(butadiene-co-styrene-co-2-vinylpyridine) latex composites and their properties [48]. T. Afshad studied conducting PP and PANI based chemical sensors [49]. K. A. Striebel *et al.* studied the Novel Nanodisperse composite cathode for Rechargeable Lithium/polymer Batteries and the applications [50]. F. Leroux *et al.* studied the electrochemical Li Insertion into conductive polymer/V_2O_5 nanocomposites. They used PP and PANI as a conductive polymer [51]. K. Ramachandran *et al.* studied the electrochemical characterization of a PP/montmorillonite nanocomposites [52]. M. Hepel prepared PP films and studied the electrocatalytical oxidation of methanol at finely dispersed platinum nanoparticles [53].

1.8 Theoretical background

A. Elemental analysis:

All the samples in this thesis are polymer and polymeric composites. From elemental analysis we can investigate all the elements contained the polymers and composites. For elemental analysis various methods can be used. Among them atomic absorption spectrophotometry is best of all. Here all the composites contains C, H and N. Except PANI all the composites contain silicon dioxide. Here Si is determined from the determination of SiO_2. This process is called Hydrofluorization method.

B. d.c. conductivity

The conductivity of polymer or polymeric composites depends on dopant level, protonation level of oxidation morphology and moisture content of the sample. Electrical resistivity of the polymer samples may be measured by two probe and four probe technique. The electrical conductivity may be measured by using ohm's law

$$E/I = R \qquad 1.8.1$$

where I is the current in amperes, E is the potential difference in volts and R is the resistance in ohms. The reciprocal of resistance is termed the conductance, this is measured in siemens (S) which is reciprocal of ohms (ohm^{-1}). The resistance of a samples of length L, and cross-sectional area A, is given by

$$R = \rho L/A \qquad 1.8.2$$

where ρ is a characteristic property of the material termed the resistivity. If L and A will be measured respectively in cm and square cm then ρ refers to cm cube of the material, and

$$\rho = RA/L \qquad 1.8.3$$

The reciprocal of resistivity is the conductivity, (formerly specific conductance)

$$K = 1/\rho \quad \text{or} \quad K = L/RA \qquad 1.8.4$$

which in SI units is the conductance of a one cm cube of substance and has the units $ohm^{-1}cm^{-1}$ or S cm^{-1} [54].

In this experiment, the solid samples are converted into pelette by pressing appropriate pressure 10^4 pounds per square inch. For electrical connection, silver paste is used on the pelette. Two electrodes of microvolt are connected with silver paste and resistivity is

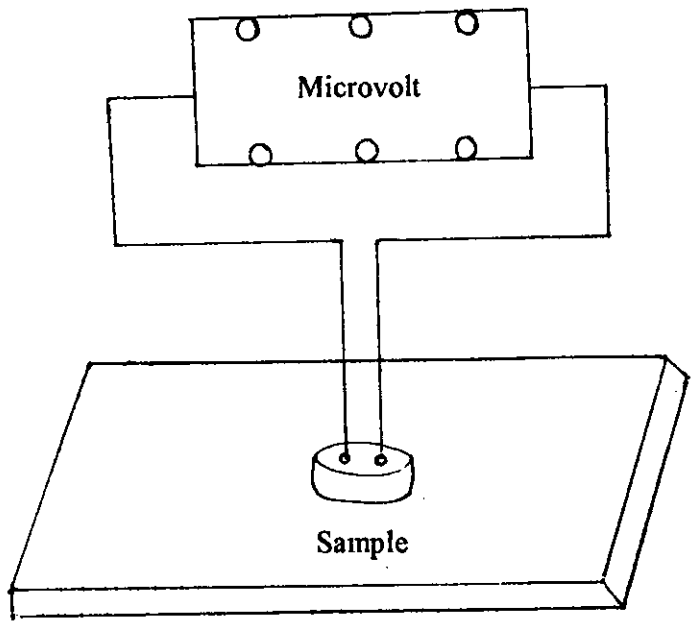


Fig. **1.8.1**: The construction for the measurement of d.c. conductivity

measured directly after some time interval. A schematic diagram of the construction for d.c. conductivity measurement is shown in Fig. 1.8.1.

C. X-ray diffraction (XRD)

The x-ray diffraction (XRD) provides substantial information on the crystal structure. This method is applied for the investigation of orderly arrangements of atoms or molecules through the interaction of electromagnetic radiation to give interference effects with structures comparable in size to the wave length of the radiation. Studies on the crystal structure developed, based on methods using single crystals after the discovery of x-ray diffraction by crystals made by the Von Laue [55]. Now a days XRD is used not only for the determination of crystal structure but also for chemical analysis, such as chain conformations and packing for polymers, for stress measurements and for the measurement of phase equilibria and the measurement of particle size, for the determination of the orientation of the crystal and the ensemble of orientations in a polycrystalline material.

X-rays are the electromagnetic radiation whose wavelength are in the neighborhood of 1°A. The wavelength of an x-ray is thus of the same order of magnetude as the lattice constant of crystals, and it is this which makes x-rays so useful in structural analysis of crystals whenever x-ray are incident on a crystal surface they are reflected from it. The reflection abides by the celebrated Bragg's law as given below:

$$2d\,Sin\theta = n\lambda \qquad 1.8.5$$

where d is the distance between crystal planes, θ is the incident angle, λ is the wave length of x-ray and n is a positive integer.

The diffracted x-rays may be detected by their action on photographic films or plates or by means of a radiation counter or electronic equipment feeding data to a computer [56].

The main purpose of using this technique in the anlysis of conducting polymer colloids such as PANI, PANI /silica, CH_3- PANI /silica and Cl- PANI /silica is to observe, from the x-ray diffraction pattern, the change in crystallinity in the series upon same condition.

D. Infra-red spectroscopy

Emission or absorption spectra arise when molecules undergo transition between quantum states corresponding to two different internal energies. The energy difference ΔE between the states is related to the frequency of the radiation emitted or absorption by the quantum relation

$$\Delta E = h\nu \qquad 1.8.6$$

where h→ planck's constant, ν→ frequency. Infrared frequencies have the wave length range from 1μm to 50μm are associated with molecular vibration and vibration-rotation spectra. Detection of chemical groups and bonding are done by the typical spectra.

In polymers the IR absorption spectrum is often surprisingly simple, if one considers the numbers of atoms involved. This simplicity results first from the fact that many of the normal vibrations have almost the same frequency and therefore appear in the spectrum as one absorption band and, second, from the strict selection rules that prevent many of the vibrations from causing absorptions. In our

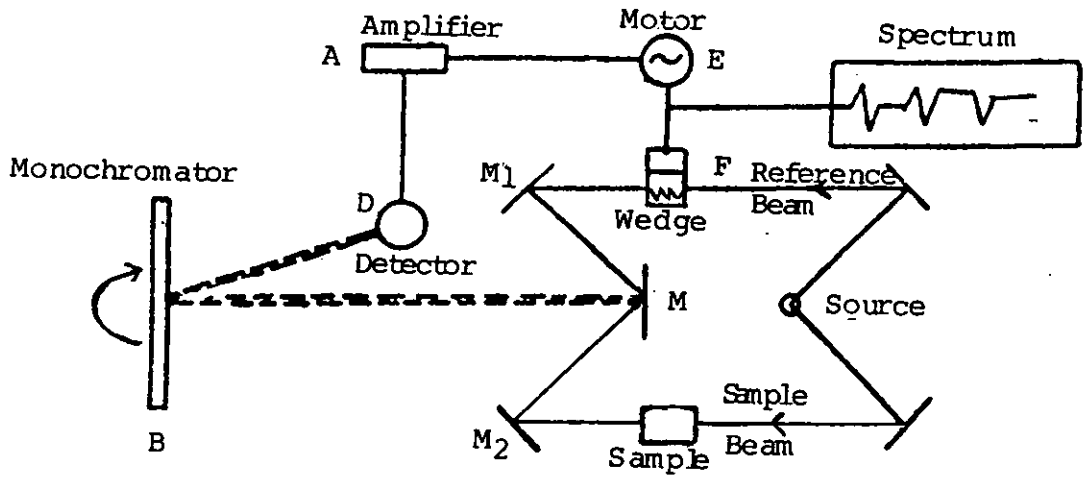


Fig. 1.8.2 : A block diagram of an IR spectrophotometer

experiment, we try to observe the change in frequency of different samples and detection of SiO_2 by following the Si-O or O-Si-O frequencies. Infrared spectrum of all the compounds were recorded on IR spectrophotometer in the region of 4000-400cm^{-1}. Samples were introduced as KBr pellets. A block diagram of an IR spectrophotometer is shown in Fig. 1.8.2.

E. Ultraviolet-visible(UV-VIS) spectroscopy

Electromagnetic radiation of suitable frequency can be passed through a sample so that photons are absorbed by the samples and changes in the electronic energies of the molecules can be brought about. So it is possible to effect the changes in a particular type of molecular energy using appropriate frequency of the incident radiation. When a beam of photons passes though a system of absorbing species, then we can write

$$-\frac{dI}{dx} = \alpha I \qquad 1.8.7$$

where, I→ intensity of photon beam

dI→ reduction of intensity

dx→rate of photon absorption with distance (x) traversed

α→absorption co-efficient of the material

Now if I_o is the initial intensity at thickness l = 0 and I is the transmitted radiation at x = l, then by integration, we can write

$$ln\frac{I_o}{I} = \alpha l \qquad 1.8.8$$

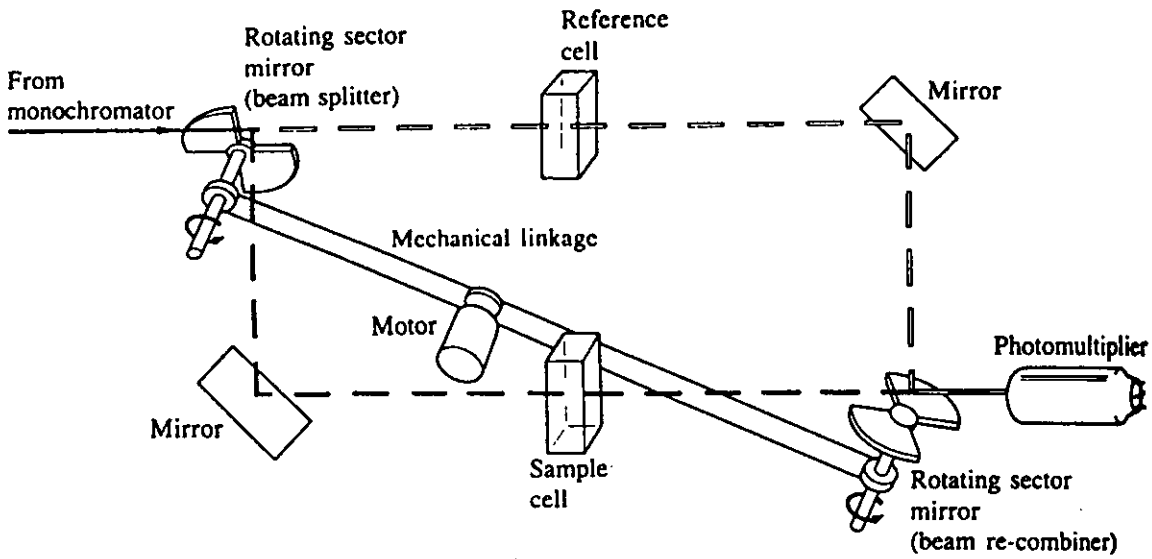


Fig. 1.8.3: A block diagram of an UV-Vis spectrophotometer

For polymers and polymeric composites, UV-VIS spectrum is taken to measure the impurity level, band gap energy etc. The electronic spectra of the prepared compounds were recorded on a UV-VIS recording spectrophotometer in the wave length range 200-1100nm. A schematic diagram of UV-VIS spectrophotometer is shown in Fig. 1.8.3.

F. Electrochemical measurement

Electrochemical process is widely used in the polymerization of organic polymer. Most of the system for electrochemical polymerization consists of compartment where three electrodes are dipped into the solution containing monomer and electrolyte and also colloidal silica solution. Appropriate potential is applied to the working electrode for polymerization of the monomers. The potential of the working electrode, where deposition of the polymer film takes place, is controlled versus the reference electrode using a feed-back circuit or a potentiostate. Feed-back circuit drives the current between the working and counter electrode while ensuring that non passed through the reference electrode circuit.

The nature of the working electrode is a critical consideration for the preparation of these films. Since the films are produced by an oxidative process, it is important that the electrode is not oxidized concurrently with the aromatic monomer. For this reason, most of the available films have been prepared using a platinum or a gold electrode. However, a variety of semiconducting materials, including tin oxide, n-type silicon, gallium arsenide, cadmium sulfide and cudmium selenide are used as working electrode.

Potentiostatic, galvanostatic and potential sweep techniques such as cyclic voltametry are widely used for electrochemical polymerization of aromatic

compounds. In potentiostatic technique a constant potential is applied to the working electrode which is sufficient to oxidize the monomers to be polymerized on the electrode. In galvanostatic process a constant current density is maintained to polymerize the monomers while film thickness can be monitored in the similar way as described for potentiostatic technique. On the other hand, cyclic voltammetry involves sweeping the potential between potential limits at a known sweep rate. On reaching the final potential limit, the sweep is reversed at the same scan rate to the initial potential and the sweep may be halted, again reversed, or alternatively continued further. In such experiments cell current is recorded as a function of the applied potential.

G. Adsorption study

Adsorption is a surface phenomena. Adsorption may be defined as a process in which the concentration of a chemical species is greater on the surface than in the bulk resulting from in elastic collision suffered by molecules on the surface. The species that is adsorbed is called adsorbate and the material of the surface is called adsorbent. Adsorption strictly refers to accumulation of adsorbate on the sruface only due to residual field of force.

The adsorption surface is generally a solid or liquid. Surface of solids or liquids have certain properties and characteristics that make them different from the bulk of matter. Although there is no chemical distinction between the molecules or atoms on the surface and the molecules or atoms in the bulk, energy considerations lead to quite dissimilar properties.

When two immiscible and chemically non reactive phases are brought into contact with each other, adsorption is a common observation which means that the

concentration of one phase is greater at the interface than the bulk. This occurs due to unsaturation of the surface atoms. Most studies of adsorption from solution have been concerned with equilibrium conditions and predominantly with the adsorption isotherm. In almost all studies of adsorption by solids from solution which results from adsorption. Generally two types of adsorptions have been distinguished : (a) Physical adsorption (Physisorption) and (b) chemical adsorption (chemisorption). Physical adsorption results purely from physical forces like vander waals forces and chemical adsorption is due to formation of chemical bonds.

H. Optical microscopy

In comparison with a biological microscope, the optical one differs in the manner by which the specimen is illuminated [57]. In optical microscope, a horizontal beam of light from some light source is reflected, by means of a plane-glass reflector, downward through the microscope objective onto the surface of the specimen. Some of this incident light reflected from the specimen surface will be magnified in passing through the lower lens system, the objective, and will continue upward through the plane-glass reflector and be magnified again by the upper lens system, the eyepiece. The initial magnifying power of the objective and the eyepiece is usually engraved on the lens mount. When a particular combination of objective and eyepiece is used at the proper tube length, the total magnification is equal to the product of the magnifications of the objective and the eyepiece.

The maximum magnification obtained with the optical microscope is about 2000x. The principal limitation is the wavelength of visible light, which limits the resolution of fine detail in the optical specimen. The magnification may be extended some what by the use of shorter-wave length radiation, such as

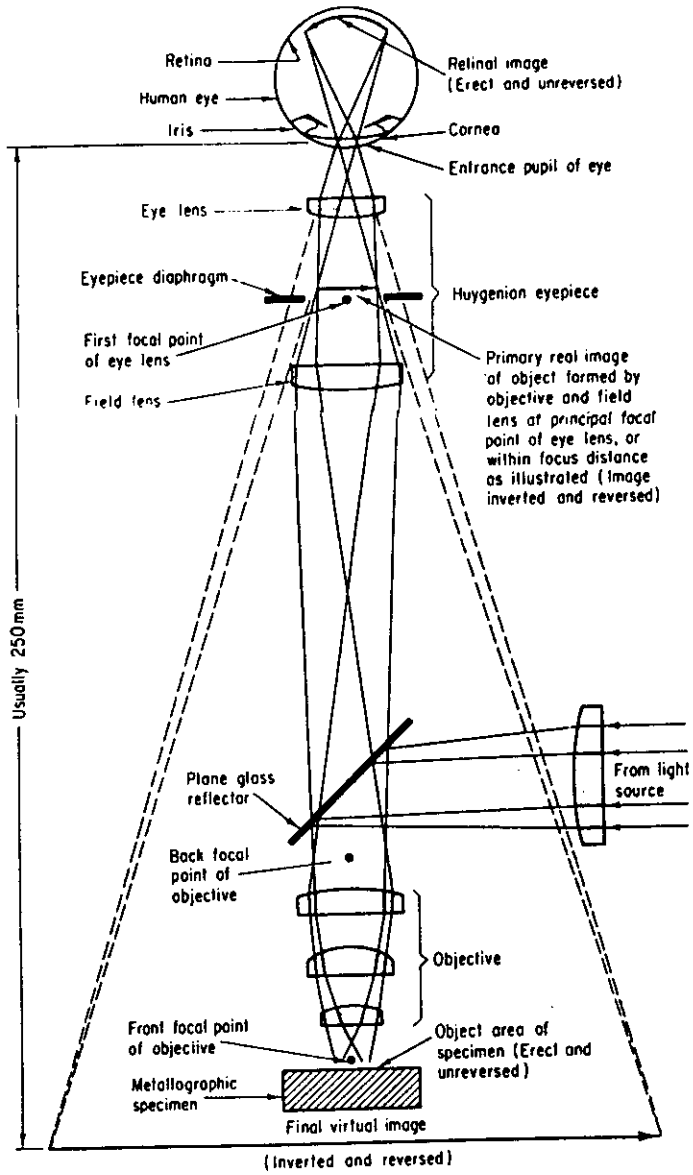


Fig. 1.8.4: Illustrating the prenciple of the optical compound microscope and the trace of rays through the optical system from the object field to the final virtual image.

ultraviolet radiation, but the sample preparation technique is more involed. The specimen is polished and etched following normal metallographic practice before taking photograph. In the optical microscope the image is brought into focus by changing the lens spacing. Fig. 1.8.4 illustrates the principle of the optical compound microscope and the trace of rays through the optical system from the object field to the final vitual image.

I. Determination of particle size

Particle size of any sample can be determined by a well known sedimentation method. Sedimentation size analysis depends on the fact that the equilibrium velocity of a particle through a viscous medium, resulting from the action of the gravitational force, is related to the size of the particle by Stokes' law. For spherical particles, Stokes' law may be expressed by

$$D = ku^{1/2} \qquad 1.8.9$$

where

$$k = \left[\frac{18\eta}{(\rho - \rho_o)g}\right]^{1/2} \qquad 1.8.10$$

and D is the diameter of the spherical particle, u its equilibrium sedimentation velocity, and ρ its density. The fluid medium is characterized by viscosity η and density ρ_o, g is the acceleration of gravity.

There are limits of applicability for Stokes law. It applies rigorously only when the relationship between particle diameter and sidimentation velocity is in conformity with

$$\frac{Du\rho_o}{\eta} < 0.3 \qquad 1.8.11$$

The left side of equation 1.8.11 is known as the Reynolds number. As long as this dimension less number is below 0.3, fluid flowing around a particle maintains a laminar pattern and Stokes law applies.

When Stokes law applies, a particle of equivalent spherical diameter D settle a distance h in time t according to

$$D = k\left(\frac{h}{t}\right)^{1/2} \qquad 1.8.12$$

Consequently after a given time interval t_i all particles larger than the corresponding diameter Di will have fallen below a given distance h from the surface of an initially uniform suspension of particles. If the initial uniform concentration of particles is Cs g/ml and the concentration after time t_i at distance h is Ct g/mt, then Pi, the wight percent of particles finer than D_i is

$$\rho_i = 100\frac{C_t}{C_s} \qquad 1.8.13$$

By obtaining values of C_i after various time the corresponding values of ρ_i and D_i may be calculated. This set of (ρ_i, D_i) data pairs when plotted yields an integral, or cummulative distribution of equivalent spherical particle diameter.

Sedigraph instruments utilize a beam of low energy x-ray to measure particle concentration in terms of the transmittance of the settling suspension relative to the initial homogeneous suspension, taking into account the transmittance of the cell walls and the suspending liquid. Transmittance of x-ray wavelengths is a function of the weight concentration of the suspended solids. The beam is made extremely small in the vertical direction and because it does not disturb the suspension, provides an ideal measuring device.

When an x-ray beam is passed through a sample container, or cell, of rectangular cross-section from a direction perpendicular to one of its sides, the fraction of the incident radiation transmitted through the cell filled with particles dispersed in a liquid is given by

$$\frac{I}{I_o} = ex\rho\left\{-\left(a_l\phi_l + a_s\phi_s\right)L_l a_c L_2\right\} \qquad 1.8.14$$

where I and I_o are the transmitted and incident intensities, a_l a_s and a_c the x-ray absorption co-efficients of the liquid, the particle solids, and the cell windows, respectively; ϕ_{lo} and ϕ_s, the mass fractions of liquid and solids present in the suspension; L_l the internal cell thickness in the direction of radiation; and L_2 the total thickness of the cell windows. By using the relationship $\phi_l = 1 - \phi_s$ and by difining transmittance T as the ratio of the transmission of the cell when filled with sample to its transmission when filled with pure suspending liquid there is obtained

$$T = \exp\{-\phi_s(a_s - a_l)\, L_l\} \qquad 1.8.15$$

or, $$\ln(T) = -A\phi_s \qquad 1.8.16$$

where A is a constant for the particular apparatus and suspension components.
By collimating the x-ray beam through horizontal slits small in vertical dimensions compared to the sedimentation dept h, the values of T measured after specific time intervals can be used in calculating the particle size distribution;

i.e. $$\rho_i = 100\frac{\ln T_i}{\ln T_s} \qquad 1.8.17$$

where T_s refers to the transmittance of the initial suspension, and ρ_i and T_i the weight percent of particles and the transmittance of the suspension after the time interval t_i [58].

Determination of Mass, Area and Number: Cumulative mass percent finer vs diameter data allow a straight forward conversion to cumulative number and cumulative area by size. For the i^{th} measurement in a series of measurements of a sample, the equivalent spherical diameter is expressed as D_i and the mass percent of particles finer than D_i is expressed by M_i. The mass percent M_{ci} within a class interval is expressed by

$$M_{ci} = M_i - M_{i+1} \qquad 1.8.18$$

where two data points (D_i, M_i) and (D_{i+1}, M_{i+1}) define the i^{th} class boundary.

The diameter D_{ci} chosen to represent the class interval may be its upper or lower bounday or may be some mid-interval value such as the advantage diameter of the class. Knowing the calculation specific volume. Vc_i (volume per gram of sample) within the i^{th} class using the definition of density as follows:

$$V_{ci} = \frac{M_{ci}}{\rho} \qquad 1.8.19$$

The equivalent volume Ve of a single spherical particle of diameter D_{ci} is calculated from solid geometry as

$$V_{ci} = 0.167^{o}\,\pi D_{ci}^{3} \qquad 1.8.20$$

The equivalent number of particles per gram contained in the i^{th} class interval is

$$N_{ci} = \frac{V_{ci}}{V_{ci}} \qquad 1.8.21$$

The equivalent area represented by a single spherical particle of diameter D_{ci} is

$$A_{ci} = \pi D_{ci}^{2} \qquad 1.8.22$$

and the equivalent specific area of particles (area per gram of sample) in the i^{th} class interval is calculated by

$$A_{ci} = (A_{ci})(N_{ci}) \qquad 1.8.23$$

1.9 Objectives of the present work

During the last two decades, a new class of organic polymers has been synthasized with remarkable ability to conduct electrical current. This class of materials are called conducting polymer. Interest in the electrical properties of highly conjugated polymers has increased rapidly during the past decade. In the early 1980s existment ran high when several prototype devices based on conductive polymers, such as, rechargable batteries and current rectifying p-n junction diodes were announced. Conducting polymers such as PANI, PP and PT are excellent candidates for numerous applications such as display devices, sensors and microelectronic devices beause they show intriguing electrical, electrochemical and optical properties. Most of these applications require repeated injection and removal of charge from the polymer by doping and undoping processes. The doping process, which is accomplished by the oxidation of polymer, produces positively charged polymeric species that are susceptible to the nucleophilic attack by electrolytes and/or solvents, resulting in the gradual degradation of the polymer. In addition, conducting polymers are almost insoluble in any known solvents. Unfortunately, poor stability and limited processibility of the conducting polymers have emerged as a major obstacle to their commercial break through. In recent years considerable research activity has focused on developing novel processable forms of relatively air-stable conducting polymers such as PP and PANI. One approach is the preparation of colloidal dispersion of such materials. The objectives of the present work are as follows:

(i) to establish a method for synthesizing conducting polymer colloid

(ii) to establish a process for the electrosynthesis of organic polymer/silica composites

(iii) to investigate surface properties of the synthesized materials

(iv) to study stability of the polymer colloid

(v) to study structural, optical and electrical properties of the synthesized material.

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CHAPTER 2

EXPERIMENTAL

2.1 Materials

All the chemicals and reagents used in this work were analytical grade. Aniline, o-toluidine and 2-chloro aniline were used as monomers. Aniline and o-toluidine were purchased from E. Merk, Germany while 2-chloro aniline was obtained from BDH Chemicals Limited, England. All the three monomers were purified by double distillation prior to their use and stored in the tight glass containers. Hydrochlolric acid (32%), sulfuric acid, hydrofluoric acid, dimethyl formamide (DMF) and ammonium peroxy disulfate, $(NH_4)_2S_2O_8$ (98%) also from E. Merck, Germany were used as received. Silica (granule size) used in preparing the composite materials were obtained from BDH Chemicals Limited, England. Doubly distilled water was used as solvent to prepare all solutions required in this work.

2.2 Synthesis of conducting polymer colloids: PANI/silica composite

(A): Chemical synthesis

Synthetic procedure was followed as described in detail elsewhere for the preparation of PANI/silica [1-3] composites. Preparation procedure is as follows: Aqueous colloidal suspension of silica was prepared by adding 2.0 g of silica particles to distilled water followed by beating the mixture with a homogenizer for two hours. The resulted dispersion was then allowed to settle for two hours. During this span of time relatively bigger silica particles were sedimented at the bottom of the container. The smaller particles remains in the system and dispersed colloidally. The colloidal solution was then decanted and used for PANI/silica composite preparation.

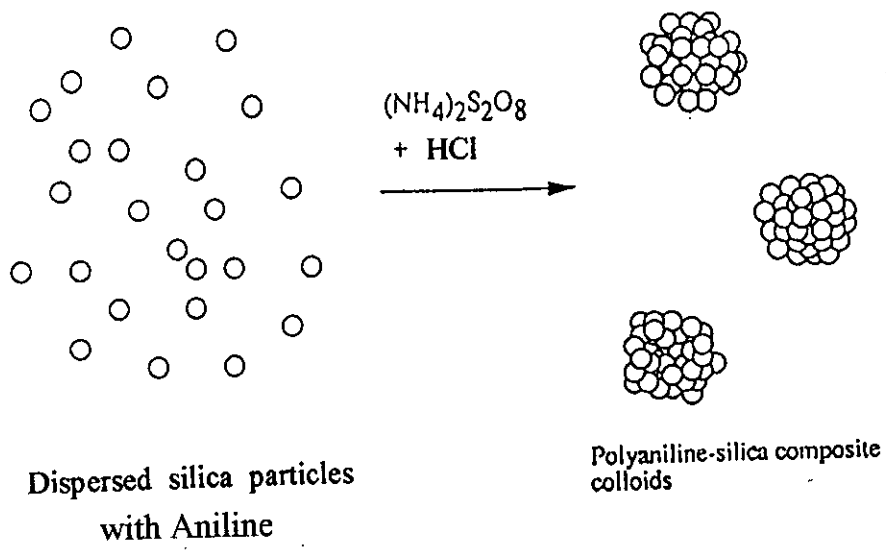

Fig. 2.1: General scheme for the preparation of polymer/silica composite colloids

2.5 ml of aniline, 5ml of HCl and 3.0 g of $(NH_4)_2S_2O_8$ were then added to the 400 ml of the prepared aqueous suspension of colloidal silica at room temperature. The polymerization was allowed to proceed for over night. The reaction mixture was then centrifuged for 6000 rpm for 30 minutes and the resulting deep blue sediment was redispersed in distilled water. The centrifugation-redispersion cycle was repeated thrice or more in order to remove completely the excess small silica particles from the larger PANI/silica composite. A schematic representation for the preparation of PANI/silica composite colloids is shown in Fig. 2.1. CH_3-PANI/silica and Cl-PANI/silica have also been synthesized following the same procedure discribed above. Here a centrifuge machine (Universal 16 A, Hettich, Germany) was used for centrifugation.

(B) Electrochemical synthesis

In this method composites were prepared by electropolymerizing the monomers from an electrolytic solution containing colloidal silica particles. Electrochemical polymerization of aniline, o-toluidine and 2-chloro aniline and doping of the respective polymers were done in a single compartment cell having three electrodes viz. working (WE), counter (CE) and reference (RE) electrodes. A schematic representation of the electrochemical cell used in this investigation is illustrated in Fig. 2.2. The potential of the working electrode is controlled versus the reference electrode using a potentiostat. Electropolymerization of the monomers were carried out either potentiostatically or by potential scanning on a platinum (Pt) or indium-tin-oxide(ITO) glass electrode. A saturated calomel electrode(SCE) and a Pt foil were used as the reference and counter electrodes, respectively. Massive and free standing composite film was obtained when the composition of the electrolytic solution was maintained as: 1M HCl + 0.5 M monomer in 200 ml. aqueous silica suspension.

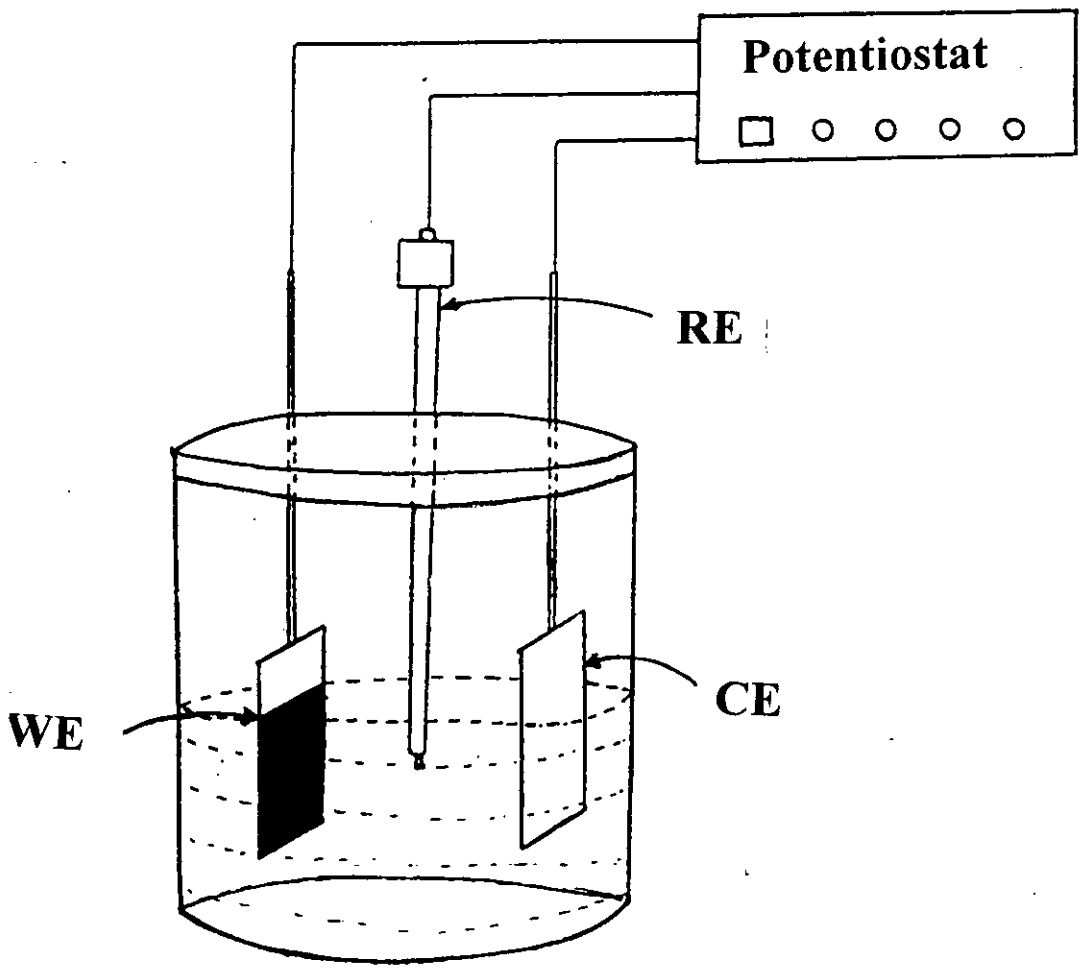

Fig. 2.2: Schematic representation of the three electrode system for electropolymerization

After synthesis, the materials were washed with distilled water several times to remove any tracess of the electrolytic solution or silica. The washed samples were then immediately kept in a vacuum desiccator at least 24 hours for drying. Synthesis of the samples employed a potentiostat (HAB-151, Hokuto Denko Ltd. Japan) while the cyclic voltammograms were recorded in a X-Y recorder (Riken Denshi Co. Ltd, Japan). All the electrochemical investigations were carried out at the room temperature.

2.3 Analysis for silica content

PANI/silica, CH_3-PANI/silica and Cl-PANI/silica were analysed for their silica content. This was done by the well known hydrofluorizatin method [4]. 1 g of the sample was taken in a crucible to which 10 ml of HF solution and 1 ml of sulfuric acid solution (1:1) were added. The crucible with lid was placed on a sand bath for evaporation of silica as SiF_4, taking care to avoid loss by sputtering. The crucible was cooled, the side of the crucible washed down with water and 2 ml of the HF solution was added and the contents were evaporated to dryness. The residue was heated on a hot plate until fumes of sulfuric acid were no longer evolved and then heated in a furnace at 120°C ± 20°C for 15 minutes. Then the crucible with the residue was cooled in a desiccator and weighed. The operation of heating, cooling and weighing were reported until the difference in mass between two successive weighing did not exceeded 0.5 mg. The difference between this mass and that of the original sample was calculated as a percentage of the mass taken.

Calculation:

$$\%SiO_2 = \frac{w_1}{w_2} \times 100$$

where, w_1 = weight of residue

w_2 = weight of loss of ignition

2.4 d.c. conductivity

Conductivities of the chemically synthesized polymer/silica composites were measured in their solid states employing conventional two probe method. For this purpose, PANI/silica, CH_3-PANI/silica and Cl-PANI/silica samples were synthesized following the procedure described in section 2.2. Synthesized samples were pressed with high pressure to form an uniform pellet having a diameter 7mm and thickness 3mm each. With this state of the rigid composite pellet, conductivity measurements were performed. An auto ranging microvolt (Keithley 197A, USA) was employed to get the voltage drop between the arbitrary two points on the pellet samples. The distance between the two points for all the samples were constant for the measurements. Electrical contacts to the points were made by conducting silver paste. The observed resistance for each sample was read directly from the microvolt equipement and allowed to calculate the specific conductance of each polymer/silica composite sample by using the relation (1.8.4) presented in chapter 1. Conductance measurements were performed under ambient atmospheric conditions.

2.5 IR spectral analysis

For IR measurement various polymer/silica composite samples were made chemically and electrochemically as the procedure described in section 2.2. Electrochemically prepared PANI/silica were deposited on a Pt electrode at a constant potential of 1.0 V vs SCE.

IR spectra of all the dried bulk polymer and polymer/silica composites were recorded on a IR spectrophotometer (IR-470, Shimadzu, Japan) in the region of 4000 - 400cm^{-1}. IR spectra of the solid samples were frequently obtained by mixing and grinding a small amount of the materials with dry and pure KBr. Thorough mixing and grinding were done in a morter by a pestler. The powdered mixture was then compressed in a metal holder under a pressure of 8-10 tonnes to make a pellet. The pellet was then placed in the path of the infra-red beam for measurements.

2.6 UV-VIS spectral analysis

A double beam spectrophotometer (UV-160A Shimadzu, Japan) attached with a synchronized recorder was employed for the UV-VIS spectral analysis of the various samples prepared chemically and electrochemically.

About 1 mg of the chemically prepared samples were dissolved in DMF. The sample solution was diluted with DMF to a visual extent in such a way that the optical density did not exceed 2. DMF was used as reference solvent in this experiment. Optical analysis for the electrochemically prepared PANI/silica sample has been performed as follows: a very thin film of the composite was electrochemical deposited on ITO glass electrode at a constant voltage of 1.0 V vs SCE. The washed and dried ITO/composite film substrate was then placed in the

spectrophotometer for the measurement. In this case, a bare ITO substrate was used as reference.

2.7 X-ray diffraction study

Chemically prepared polymer/silica composites were analysed for their x-ray diffraction pattern. For this purpose, samples were prepared as the procedure described in section 2.2. The powdered samples were pressed in a square aluminium sample holder (40mm × 40mm) with a 1 mm deep rectangular hole (20mm × 15mm) and pressed against an optically smooth galss plate. The upper surface of the sample was labeled in the plane with its sample holder. The sample holder was then placed in the diffractometer.

X-ray diffraction pattern were recorded on a automatic X-ray diffractometer (JDX-8P, JEOL Ltd., Japan) using Mo(Zr) radiation of wave length 1.54Å. The diffractometer was operated at 30KV and 20mA. The scan speed was $2^{\circ}min^{-1}$.

2.8 Optical microscopic analysis

Optical microscopic analysis for the chemically synthesized PANI, PANI/silica, CH_3-PANI/silica and Cl-PANI/silica was performed. For this purpose, samples were compressed to rigid pellets for analysis. Prior to take the micrographs, all the pellet sample's were polished to have a clear and representative view of the samples microstructure. Polishing was accomplished with emery papers viz. No. 3, No. 2, No. 1, No. 0, No. 0-0, No. 0-0-0 and No. 0-0-0-0. In addition to this, wheel polishing with γ-Al_2O_3 powder was also carried out to have better micrograph.

After polishing, the samples were cleaned off with dry cotton to remove any traces of polishing materials. Analysis were performed in an optical microscope (SWIFTMASTER II, Swift Instruments, Inc, Japan) coupled with a very high precision canon camera. All the analysis were carried out at room temperature.

2.9 Particle size determination

The particle size of the samples was determined by the well known Sedimentation method [5]. For this purpose, at first the sample was grinded and sieved by a 400 mesh sieve. The density of the powdered sample was then determined. Knowing the density of the studied specimen about 2.0 g of the sieved powdered sample was taken in a beaker. Then 80 ml of freshly prepared solvent (water) is added to the sample. The sample was stirred well to make a dispersed solution. The dispersed sample solution was introduced to the sample chamber for measurement. Particle size analysis were carried out with Micromeritrics SediGraph (model no. 5100, USA). Density measurements were performed with Micromeritics Multivolume auto pycnometer (model no. 1305, USA). A schematic diagram of SediGraph is illustrated in Fig. 2.3.

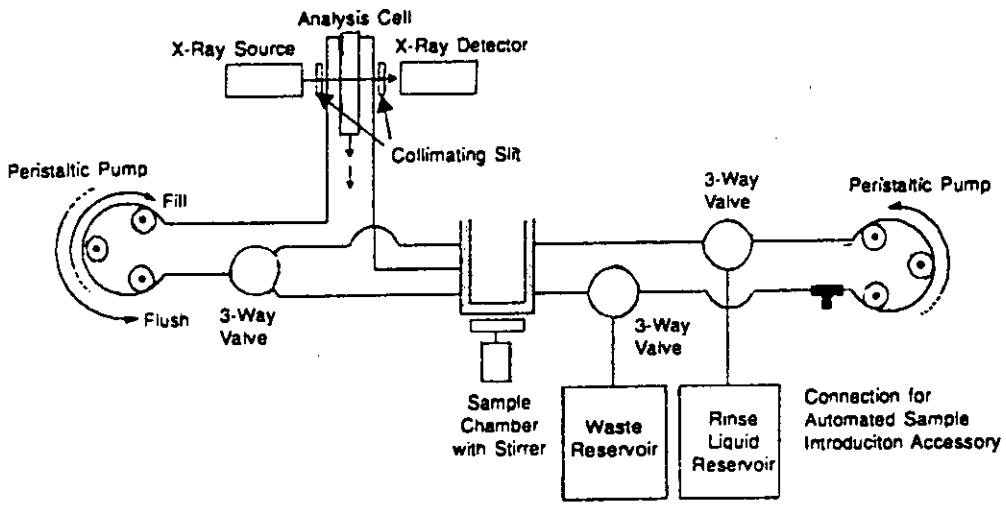

Fig. 2.3: Schematic diagram of SediGraph for particle size determination

2.10 Cyclic voltametric study

Cyclic voltammetric studies of electrochemically prepared PANI and PANI/silica samples were carried out by sweeping the potential between certain limits. For this purpose, a potentiostat coupled with an X-Y recorder was used. Cyclic voltommogram (CV) for the synthesis of PANI was performed from an aqueous solution of 0.5 M aniline and 1.0 M HCl while the same for PANI/silica was obtained from an aqueous electrolytic solution of colloidal silica, 0.5 M aniline and 1.0 M HCl. CV for doping and degradation studies were accomplished by synthesizing a film of the materials on a Pt electrode by potential sweeping between -0.2 and 1.0V. Sweeping between this range was repeated for five time to grow the material appreciably on to the surface of the Pt electrode. After washing with water several times, the Pt/film electrode was then placed in a monomer free 1.0 M HCl solution to study its doping and electrochemical degradation processes. A SCE was used as reference throughout this study. All the measurements were carried out at room temperature.

2.11 Adsorption study

Adsorption of methylene blue (MB) $C_{16}H_{18}ClN_3.3H_2O$ (reagent grade, Fluka) on PANI/silica composites were studied spectroscopically from an aqueous solution of the adsorbate. For this purpose, λ_{max} of MB was determined spectroscopically as depicted in Fig. 2.4. After that a calibration curve (absorbance vs [MB]) with different known concentration of MB was constructed to obtain any unknown concentration of MB from its absorbance data. Experimental performed for this purpose is as follows: Stock solution of MB was prepared by dissolving the known weight in distilled water. The prepared solutions were in the concentration range

*** PEAK-PICK ***

-- PEAK --		-- VALLEY --	
λ	ABS	λ	ABS
664.0	0.811	347.0	-0.052
292.0	0.371	260.0	0.053
246.0	0.132	224.0	0.031

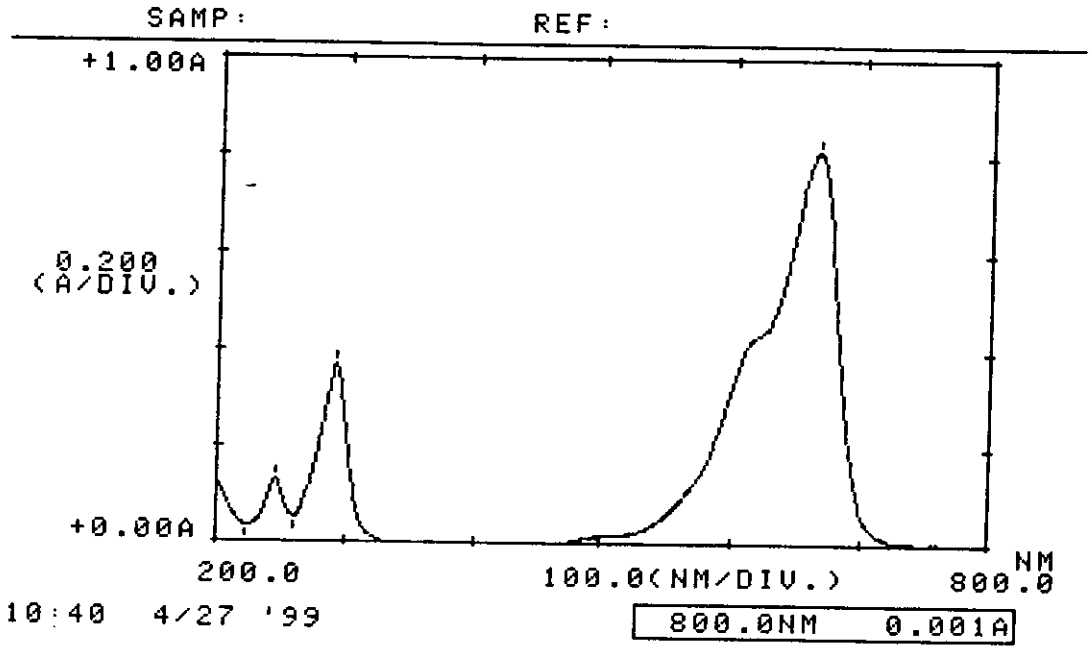

Fig. 2.4: Spectrum of an aqueous 3.0×10^{-5} M solution of MB for the determination of λ_{max}

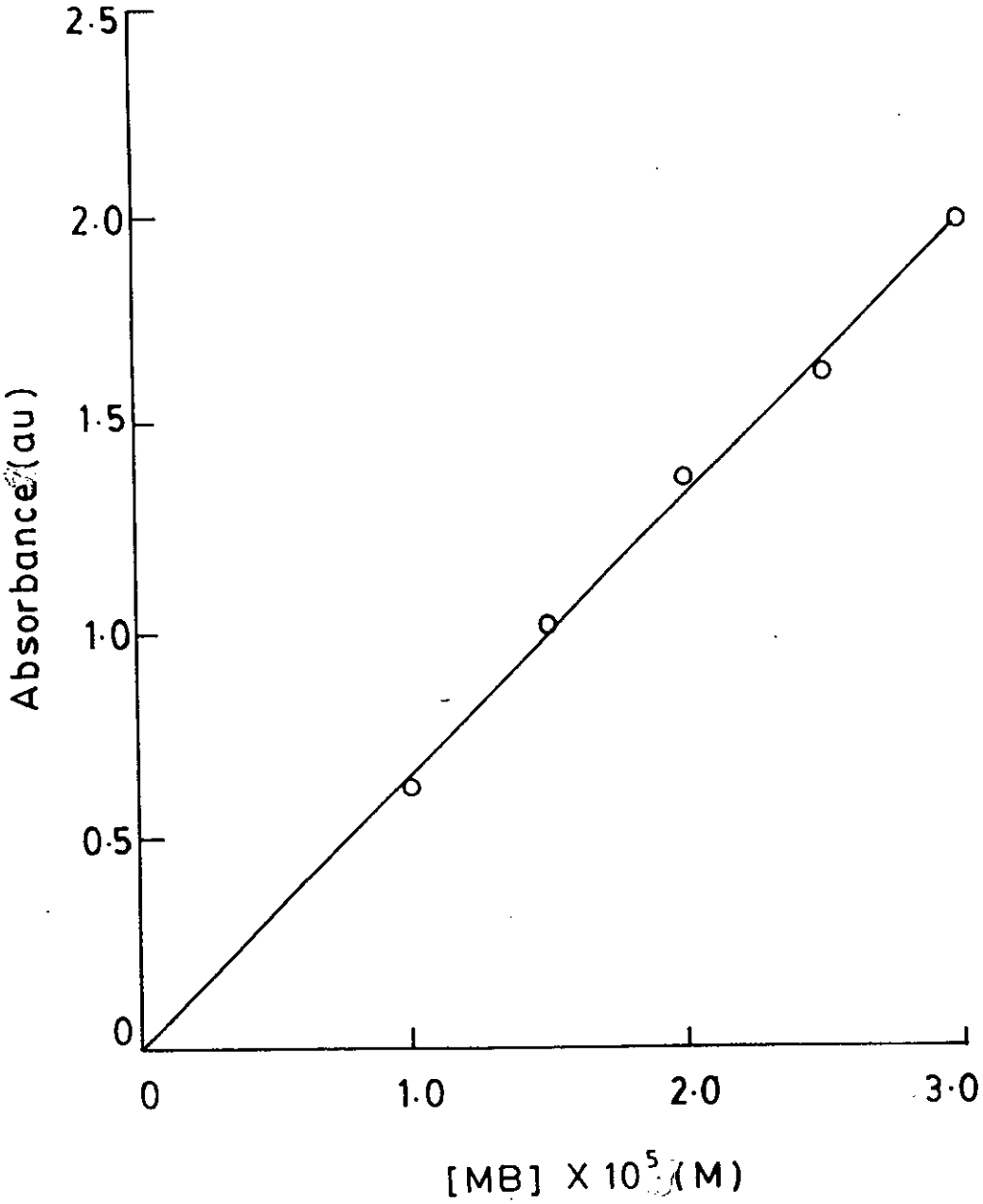

Fig. 2.5: Absorbance of MB solutions at different concentration

of 0.5×10^{-5} to 3.0×10^{-5}M. The calibration curve was constructed by plotting the absorbance of the solutions vs the concentration. The result is shown in Fig. 2.5.

A typical experiment for the adsorption of MB on PANI/silica was done in the following way: a known weight of adsorbent was taken in each of 8 bottles with stopper. 5.0 ml of water was taken in each bottle and PANI/silica sample was soaked overnight. Then 25.0 ml of 3.0×10^{-5} M MB solution was added. The bottles were shaken in a thermostated shaker maintained at 30°C. After a definite interval of time a bottle was withdrawn. The supernatant was centrifuged. The concentration of the clear solution was measured spectrophotometrically by measuring absorbance at the λ_{max} of MB. Similar solutions of other bottles were analyzed in the same way.

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CHAPTER 3

RESULTS AND DISCUSSION

3.1 Silica-stabilized conducting polymer colloids

A wide variety of oxidants is feasible in the chemical polymerization of conducting polymers: H_2O_2 [1], $FeCl_3$ [2] and $(NH_4)_2S_2O_8$ [3] are well established reagents. When aniline is oxidized in the presence of colloidal silica, colloidal PANI/silica particles of composites nature are produced. In this synthesis the precipitating PANI adsorbs as an insoluble thin layer onto the high surface area silica substrate particles. This outer layer of PANI is non-solvated and acts as a binder, effectively "gluing" the silica particles together (see Fig. 2.1). Recently, it has been reported that stable PANI colloids can be prepared in aqueous media in the presence of small silica particles i.e. using particulate rather than polymeric dispersants [4-5]. Most of the colloidal silicas have a negative surface charge. Since PANI chains are polycations (6-7), the attractive electrostatic interaction may play a certain role in the formation of PANI/silica particles.

Normally one would expect a macroscopic precipitate to be formed in these circumstances. However, under certain synthesis conditions a stable colloidal dispersion of PANI/silica composite particles is obtained. The chemical analysis of the PANI/silica colloids were performed for their silica content. The result has been shown in Table - 3.1. This analysis indicated a silica content of approximately 40% in all the chemically prepared polymer/silica composites. Each value was an average of at least three analysis. Although polymers with different functional group were used in the composite synthesis, but the result suggests that different functional groups on the bulk PANI do not have the influence on the silica content of the synthesized polymer/silica composites under investigation. The density values of the samples assessed by pycnometry using a Micromeritics have also been shown. Each value was an average of at least four rans. The density

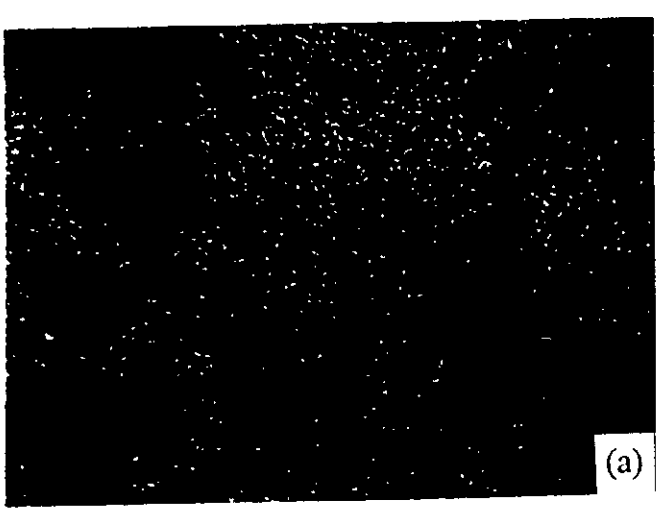
of the bulk polymer seems to be smaller than that of polymer-silica composite samples. This results seems to be reasonable since heaviour silica particles whose density is about 2.14 g cm^{-3} is incorporated to the synthesized composite matrix. Our densities data seems to be consistent with the result of the previous workers [9, 48] showing that bulk polymers exhibited lesser density than that of the polymer silica composites. This novel colloids have been characterized by optical microscope. The micrographs of the synthesized polymer/silica have been displayed in Fig. 3.1. Micrograph 3.1(a) shows the microstructure of PANI whereas Fig. 3.1(b-d) shows the microstructure of PANI/silica, CH_3-PANI/silica, Cl-PANI/silica respectively,

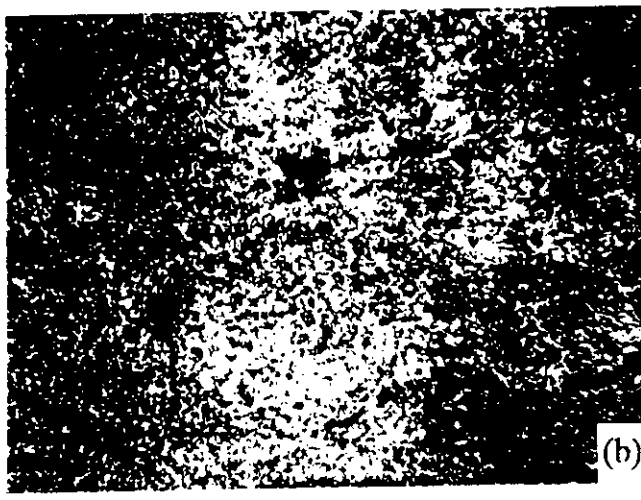
Table 3.1: Silica content and density data for the chemically synthesized samples.

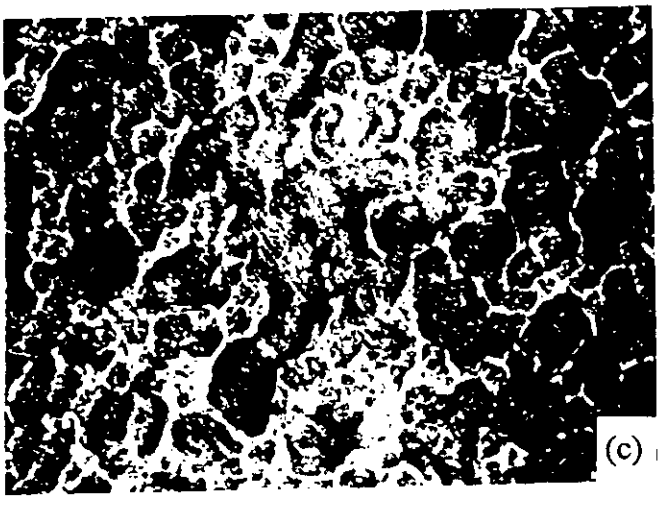
Name of the sample	Silica content (%)	density (g cm^{-3})
PANI	-	1.46
PANI/silica	40.36	1.62
CH_3- PANI/silica	38.92	1.61
Cl- PANI/silica	39.78	1.60

A wide distribution of white image can be seen in the microstructures 3.1(b-d). These image may reflect the presence of silica particles in the polymer matrix.

It may be seen that their surface composition is silica rich relative to their bulk composition, i.e. the conducting polymer component is probably somewhat depleted from the surface of the particles. This hypothesis has already been confirmed for the analogous PP/silica nano-composites using x-ray photoelectron spectroscopy [8]. Because of the limited magnification of the optical microscope, the free colloidal silica and polymer/silica particles could not be identified







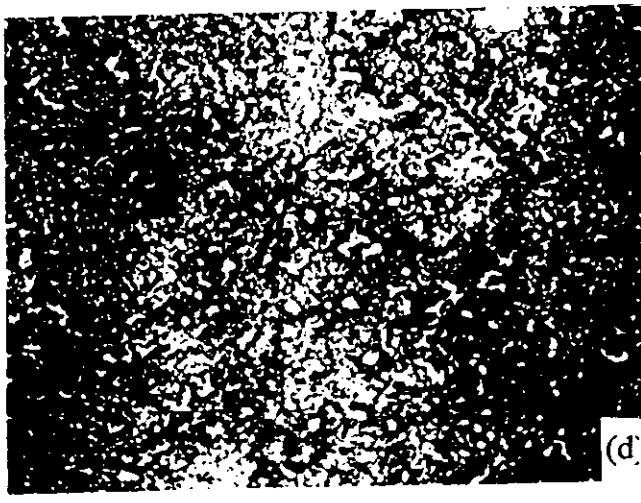


Fig. 3.1.1: Optical micrographs of the chemically synthesized (a) : PANI, (b) : PANI/silica, (c) : CH_3-PANI/silica and (d) Cl-PANI/silica (magnification : 1cm ≡ 33μm)

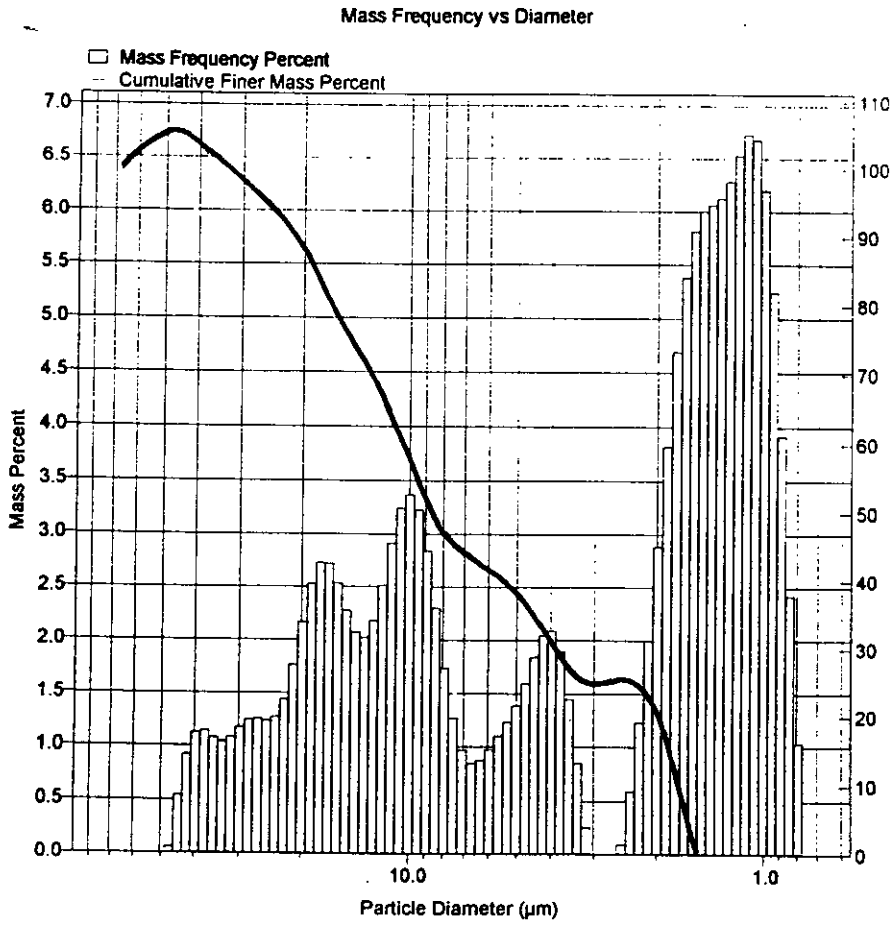


Fig. 3.1.2(a) Mass frequency vs particle diameter plot for the chemically synthesized PANI/silica.

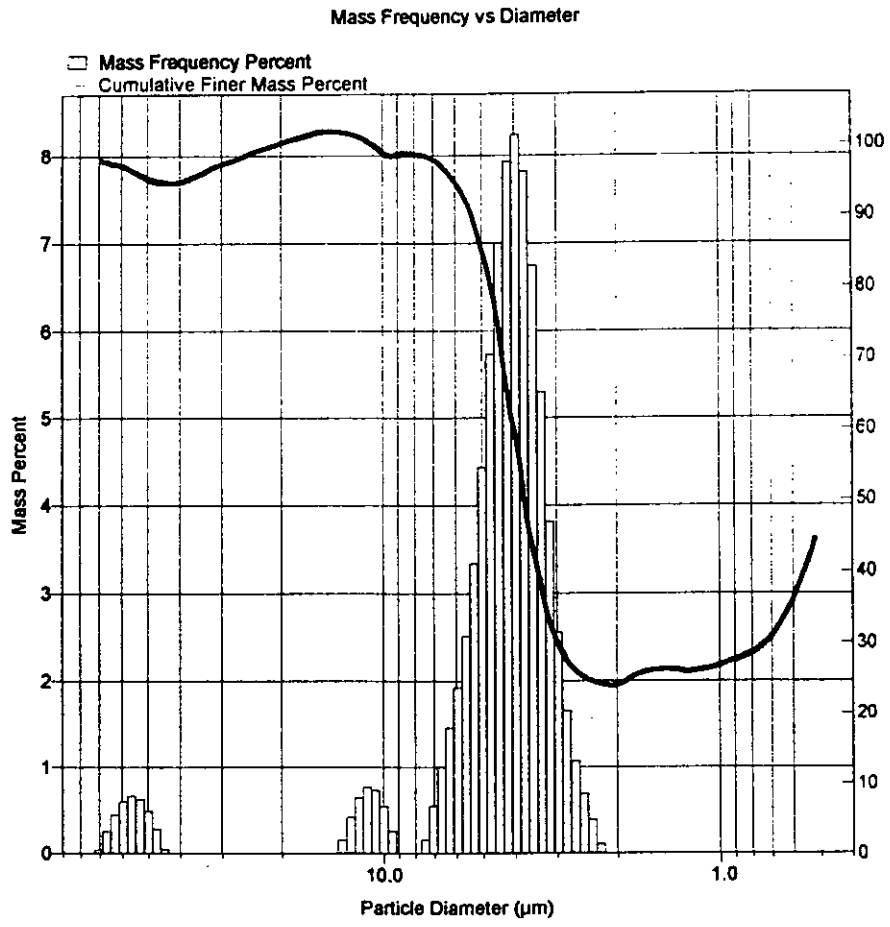


Fig. 3.1.2(b) Mass frequency vs particle diameter plot for the chemically synthesized CH_3-PANI/silica

separately. However, SEM studies of PP/silica and PANI/silica have been reported to be identified clearly the free silica and polymer/silica particles [8, 9].

Sedimentometry was our performed sizing method for composite colloids. Owing to the relatively larger density difference between polymer/silica particles and water (0.99 g cm^{-3}), this technique yields better weight average particle size distributions in short run times (20-30 mins). Typical particle size distributions for two samples are shown in Fig. 3.1.2. Considering the simple methods used in our colloidal synthesis, the observed particle size distribution is not narrow rather it shows a broad distribution, indicating the formation of the particles with a broader ranges. However, in all the cases the result shows that the majority of the particles formed are in the range of 50 - 1 μm. If their size could be reduced further, these polymer/silica matrix could prove to be interesting nanocolloids for academic studies, e.g. for studing surface phenomenon. Clearly the particle size of the PANI/silica and CH_3-PANI/silica are not similar as can be seen from the figures (Fig. 3.1.2). It is unclear at present whether the change in particle size observed with these two composites is primarily due to the differences in their polymerization kinetics or to the nature of the pre-adsorbed species on the silica particles.

3.2 IR spectral analysis of chemically synthesized samples

IR spectroscopy studies were performed in order to get some useful, albeit qualitative information on chemically synthesized PANI, PANI/silica, CH_3-PANI/silica and Cl- PANI/silica. IR spectra of the samples are presented in Figs 3.2.1 - 3.2.4 while the observed and standard bands assigned for different

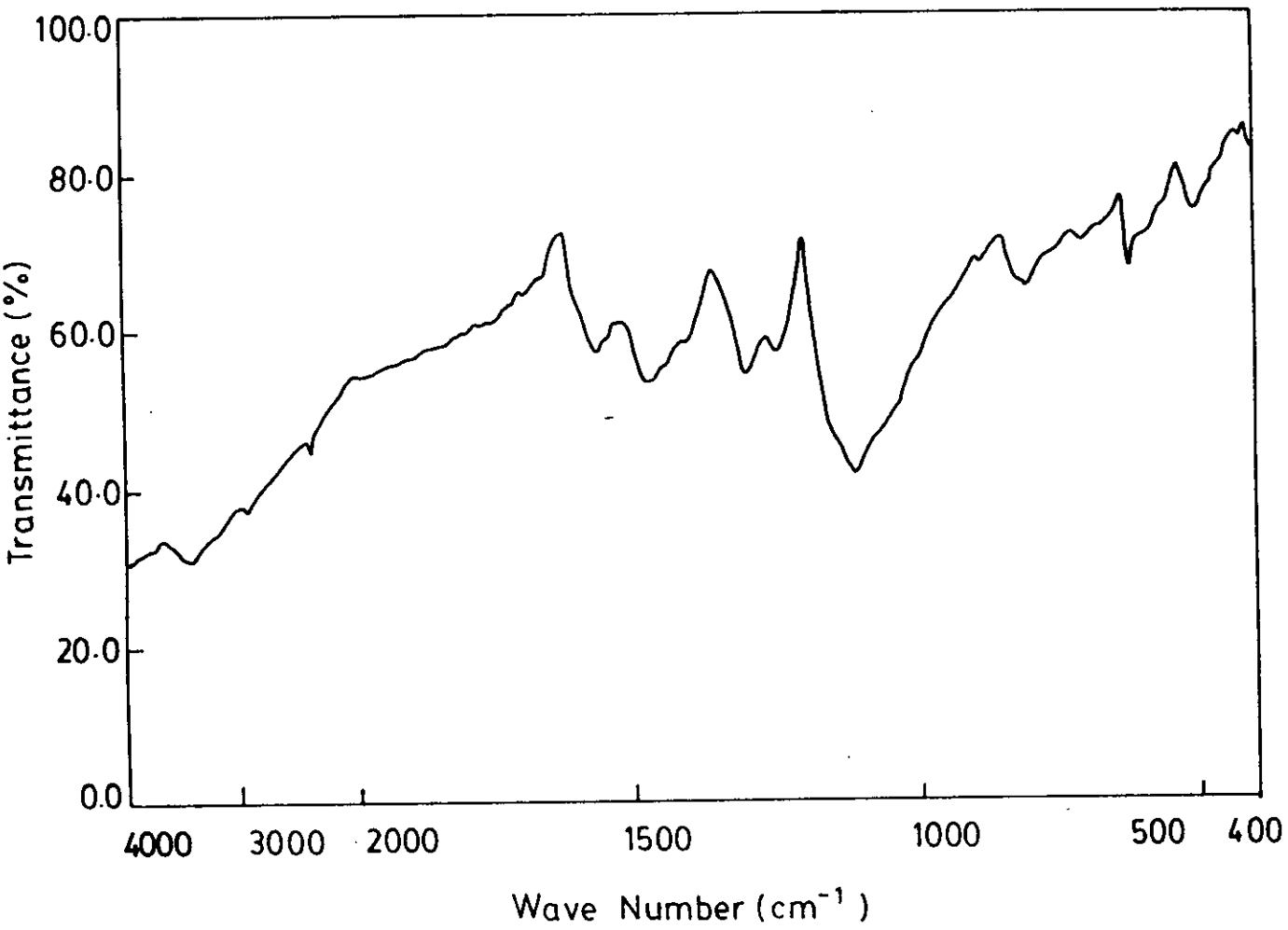


Fig. 3.2.1: IR spectrum of the chemically prepared PANI

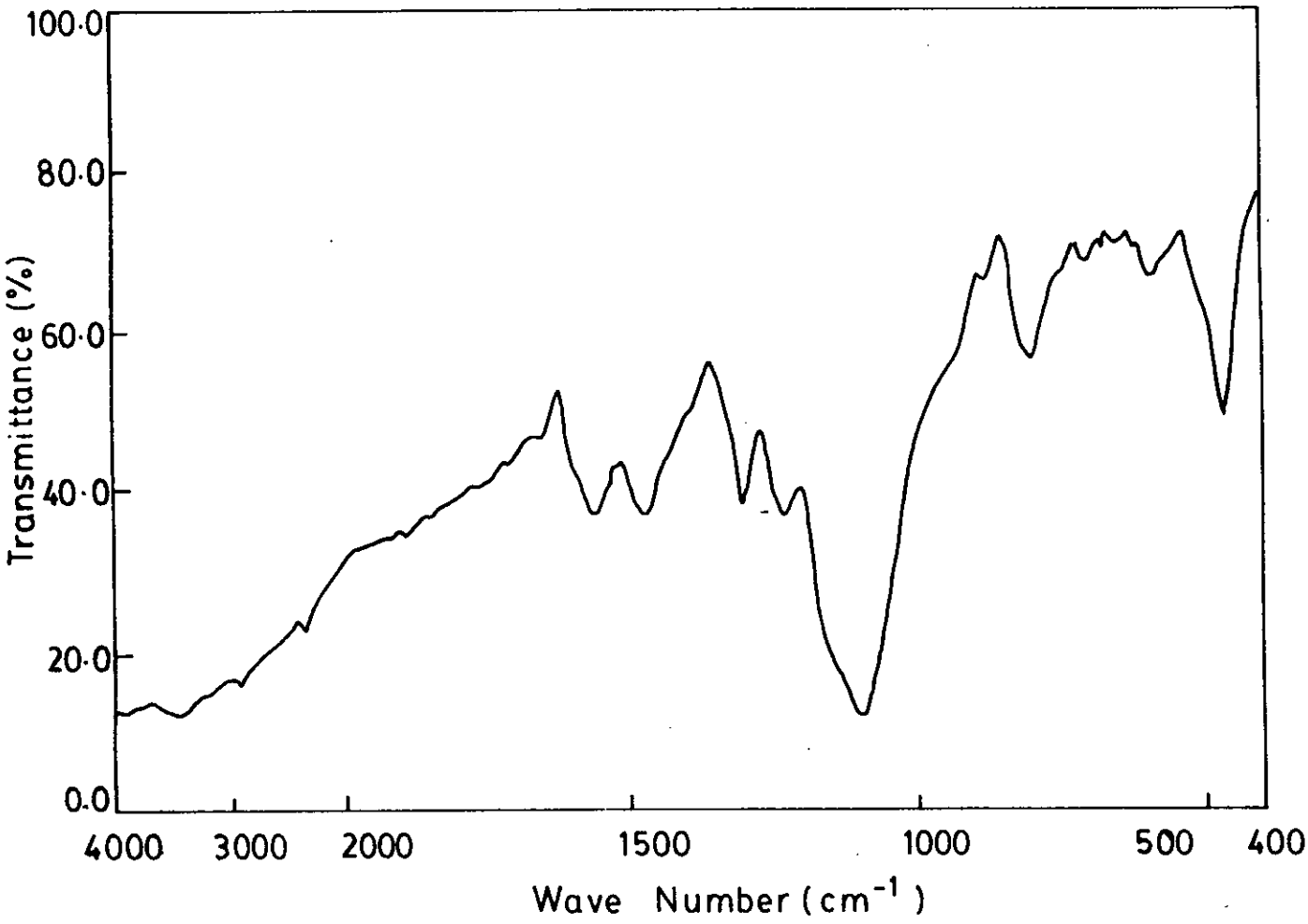


Fig. 3.2.2: IR spectrum of the chemically prepared PANI/silica.

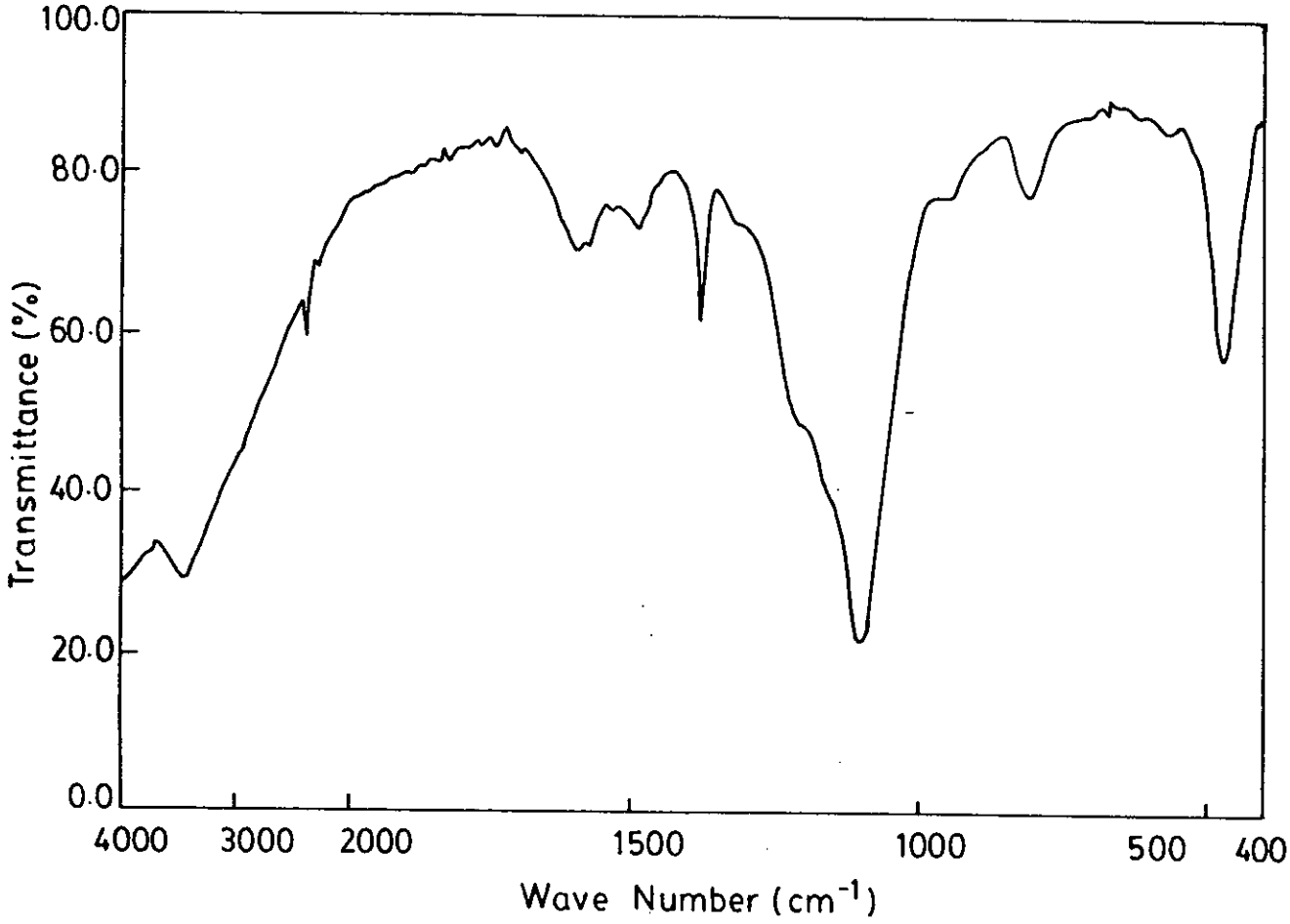


Fig. 3.2.3: IR spectrum of the chemically preparid CH PANI/silica

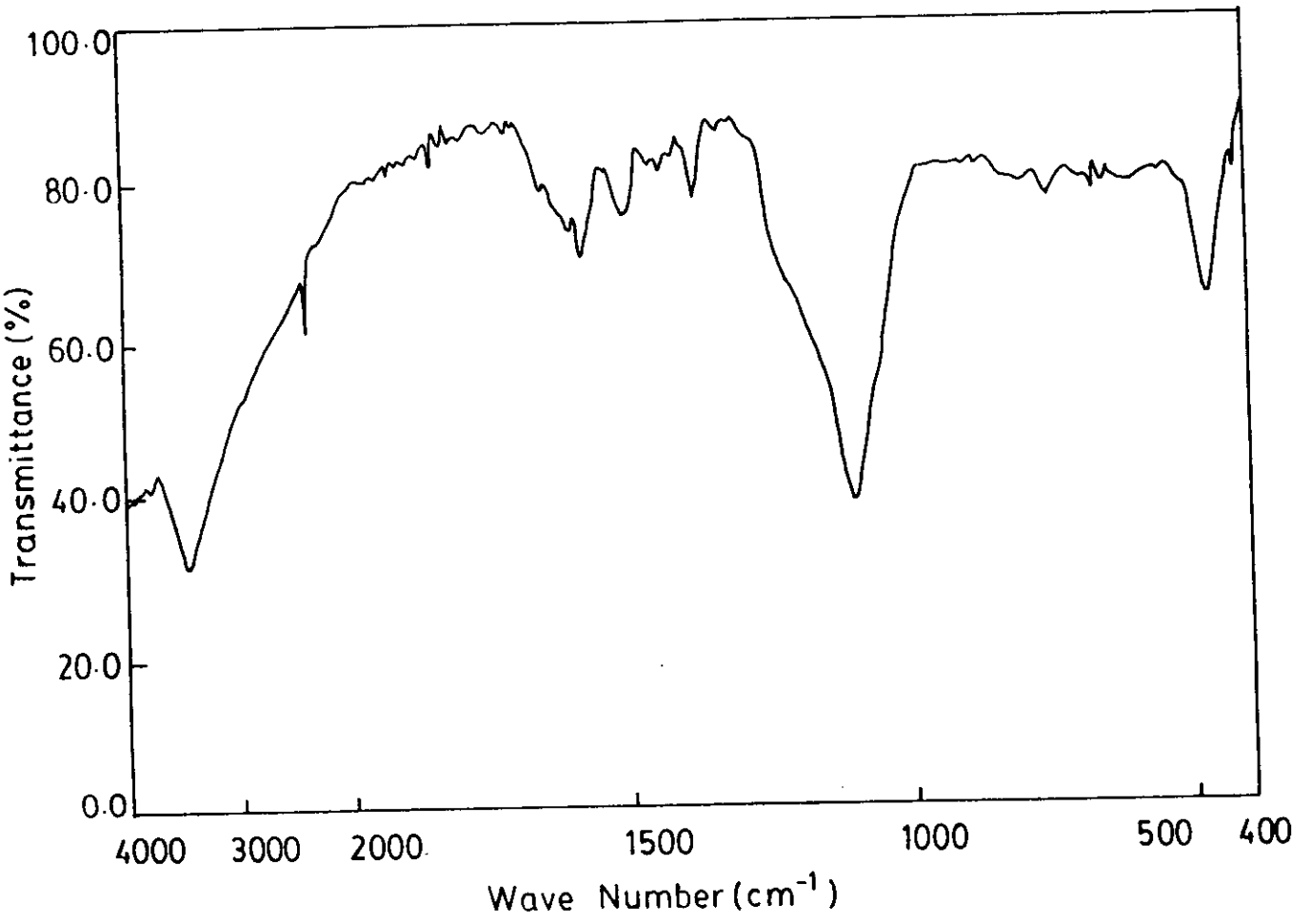


Fig. 3.2.4: IR spectrum of the chemically prepared Cl-PANI/silica

functional groups are summerized in Table 3.2. The assignment of the bands has been made on the basis of some standard literature [26-29].

Table 3.2: Observed and standard IR absorption bands assigned for different functional groups for the samples prepared chemically.

Functional groups	Standard absorption band range (cm^{-1})	Observed absorption bands (cm^{-1}) for the samples*				Probable assignment
		(a)	(b)	(c)	(d)	
Free O-H	3590-3710	3600	3665	3795		O-H stretching vibration water may be present
N-H	3300-3500	3435	3420	3480	3435	Aromatic secondary amine may be present
C=C	1600-1450	1554	1564	1591	1590	C=C stretching in aromatic nuclei
C-N	1350-1250	1295	1320	1370	1376	C-N stretching in aromatic amine
C-H	690-900	813	846	846	852, 829	C-H deformation. Monosubstituted benzene
C=N	1690-1640	1660	1676	1667	1642, 1669	=C=N stretching in imine
Si-O	801, 1111		1109, 799	1101, 801	1101, 805	presence of SiO_2
C-Cl	800-2600				668, 744	C-Cl stretching vibration in 2-chloroaniline
C-H (in CH_3)	2850-2960			2985		C-H stretching in CH_3-
Ar-H	~3030			3015		Ar-H stretching in o-toluidine

*(a): PANI, (b): PANI/silica, (c): CH_3- PANI/silica, (d): Cl- PANI/silica

Bands observed in the IR spectrum (Figs. 3.2.1 - 3.2.3) in the range 3590 - 3710 cm^{-1} may indicate water molecules that may absorbed by the samples. In fact, De Survill *et al.* [30] have observed that PANI has a strong affinity for water, its absorption capacity can be as large as 40% of the polymers weight. The peaks in

between 3300 - 3500 cm^{-1} may correspond the N-H stretching of the aromatic secondary amines. The bands in the range 1640 - 1690 cm^{-1} may be considered for C = N - stretching. It therefore, seems that the present PANI is consists of -N = sites which might occured by the high degree of oxidation of the polymer films [31]. The bands in the range 1450 - 1600 cm^{-1} and 1350 - 1250 cm^{-1} may represent C = C and C-N stretching of the aromatic amine, respectively. The bands in the region 690 - 900 cm^{-1} may provide an evidence for the mono-substitute bengene ring. This findings may indicate that the bonding in the PANI may takes place through 1, 4 - position. Besides these, the peaks at 2985 and 668 (and 744) for the IR spectrum of CH_3-PANI (Fig. 3.2.3) and Cl-PANI (Fig. 3.2.4) respectively may indicate the presence of -CH_3 and -Cl groups in the corresponding polymers. The absorption bands observed around at 801 and 111 cm^{-1} for the samples PANI/silica, CH_3- PANI/silica and Cl- PANI/silica may provide the evidence for the presence of silica. Therefore, the IR spectra of the above studies samples clearly exhibited absorption bands attributable to both the polymers and silica components.

3.3 UV-VIS spectral analysis of the chemically prepared samples

The UV-VIS spectra of chemically prepared PANI, PANI/silica, CH_3- PANI/silica and Cl- PANI/silica in DMF are presented in Figs. 3.3.1-3.3.4. The possible electronic processes that can take place under the electromagnetic UV-VIS irradiation on the studied samples have been reflected on the results. Every electronic transition is manifested as a peak in the optical spectrum.

The spectra depicted in Figs. 3.3.1 - 3.3.4 are similar to those reported for doped conducting polymers films [33]. In the doped state of PANI, a strong absorption band in the ultraviolet region is observed and the absorption in the visible region

*** PEAK-PICK ***

-- PEAK --		-- VALLEY --	
λ	ABS	λ	ABS
575.0	0.093	461.0	0.065
283.0	0.199	264.0	-0.007

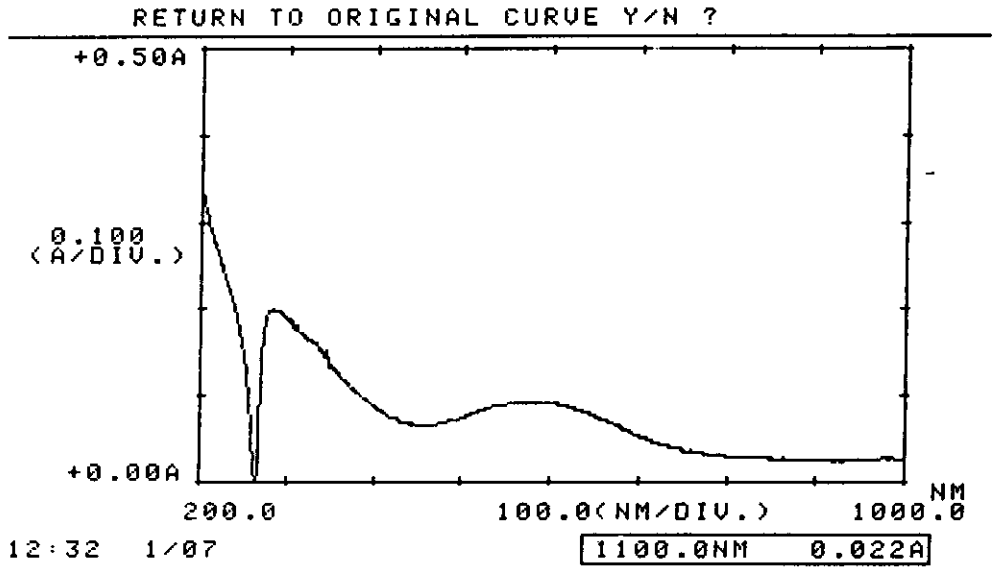


Fig. 3.3.1: UV-VIS spectrum of PANI in DMF

*** PEAK-PICK ***

-- PEAK --		-- VALLEY --	
λ	ABS	λ	ABS
284.0	0.356	753.0	0.167
		263.0	0.044

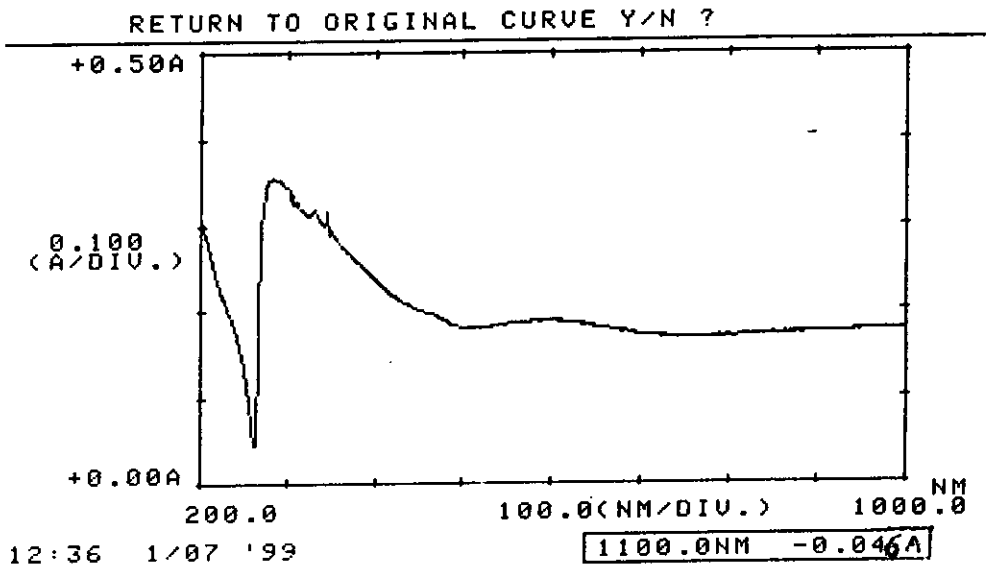


Fig. 3.3.2: UV- VIS spectrum of PANI/silica in DMF

*** PEAK-PICK ***

-- PEAK --		-- VALLEY --	
λ	ABS	λ	ABS
601.0	0.333	481.0	0.256
305.0	1.173	228.0	0.090

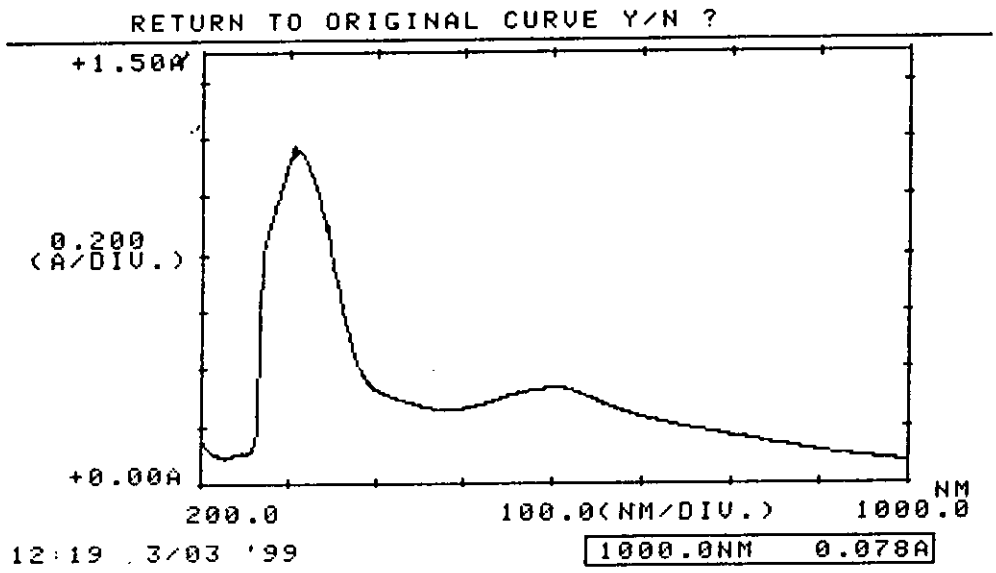


Fig. 3.3.3: UV- VIS spectrum of CH_3-PANI/silica in DMF

*** PEAK-PICK ***

-- PEAK --		-- VALLEY --	
λ	ABS	λ	ABS
344.0	2.373	307.0	1.271
275.0	1.892	221.0	0.103

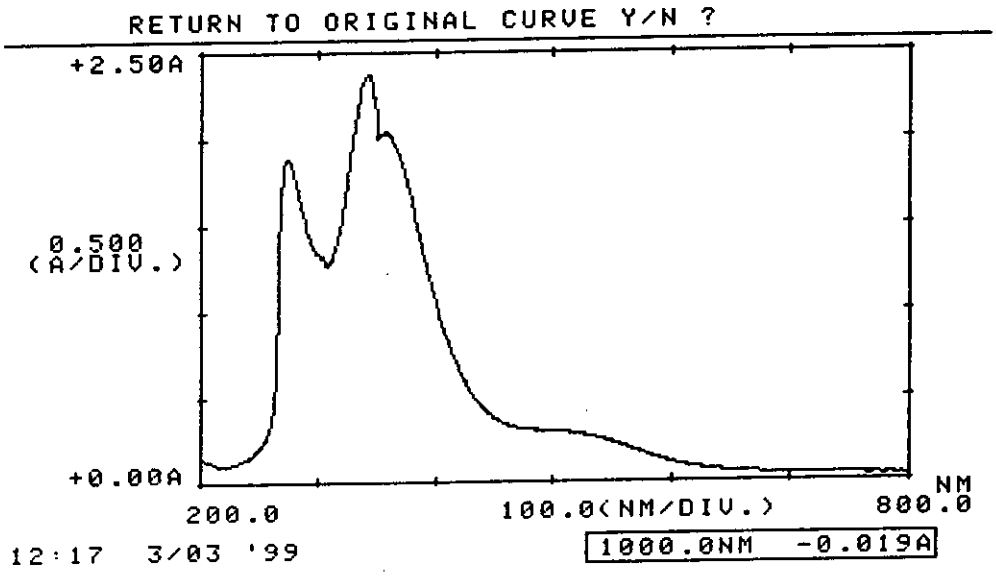


Fig. 3.3.4: UV- VIS spectrum of Cl-PANI/silica in DMF

increases when the film is doped. As the doping process occurs, the originally filled valence band of the polymer becomes partially empty. The Fermi level lowers to the valence band which ensures a metallic behaviour for the polymer. In this respect, it can be expected that the more doped the polymer will be, the more empty the valence band will become, and as a consequence that the free carriers concentration (polaron and bipolaron) and hence the conductivity will increase.

For the present samples, the peaks observed in the spectra around 283 nm (considering the tail position of the peaks) for all the studied samples may correspond the interband π -π^* (valence band to conduction band) transition. The other peak observed with all the samples at around 600 nm. This transition may responsible for the polymer conductivity by forming polaron and bipolaron as mid-gap state. Single ionization of the polymer chain results in two polaron states in the gap, one splits off from the valence band and singly occupied and a vacant state below the conduction band edge. The second charge removed comes from the already existing polaron state, forming a bipolaron, without production of additional defect state [34]. It is worth mentioning that the optical spectra of the polymer/silica samples (Figs. 3.3.2-3.3.4) are almost similar to that of bulk PANI (Fig. 3.3.1). This finding may suggests that optical and electrical properties of the bulk polymer changes hardly even incorporating silica particles in its matrix. The present optical data provided elucidation of the band-gap of the bulk PANI and PANI/silica samples. The band-gap for both the system was found almost similar and it is 4.3 eV.

3.4 X-ray diffraction pattern of the chemically synthesized samples

Both the bulk polymer and polymer/silica samples prepared chemically were examined for their structural analysis in the powdered state by using wide angle x-

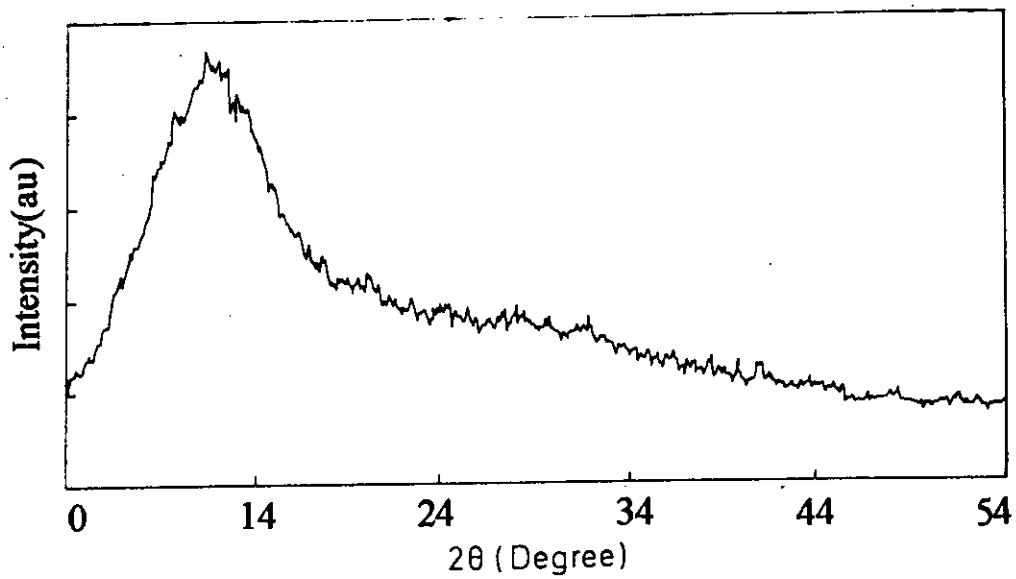


Fig. 3.4.1: XRD pattern of PANI synthesized chemically

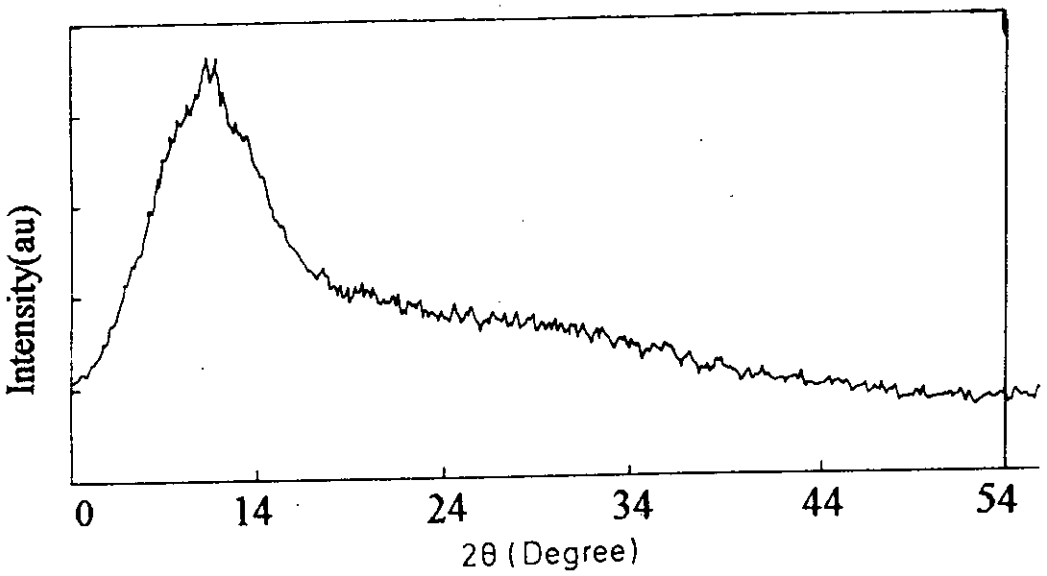


Fig. 3.4.2: XRD pattern of PANI/silica synthesized chemically

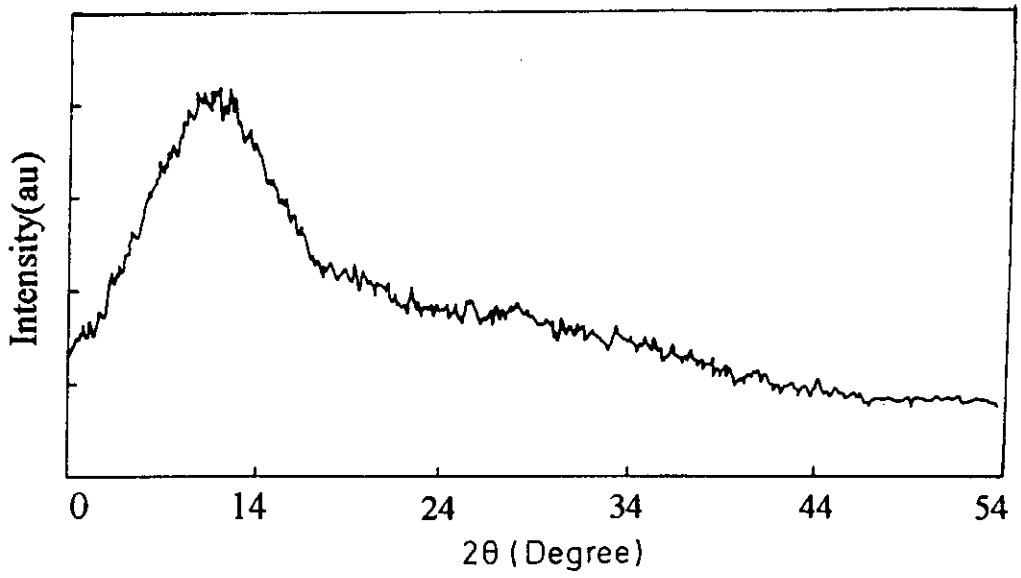


Fig. 3.4.3: XRD pattern of CH_3-PANI/silica synthesized chemically

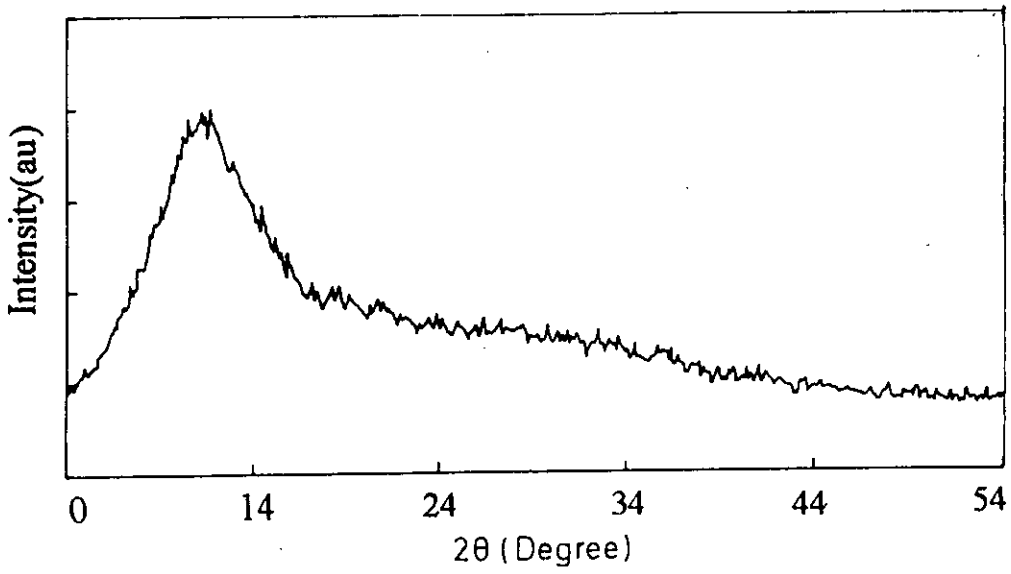


Fig. 3.4.4: XRD pattern of Cl-PANI/silica synthesized chemically

ray diffraction. The scattering patterns as a function of the Bragg angle, 2θ at λ = 1.54A° of the above samples are presented in Figs. 3.4.1 - 3.4.4.

It can be seen from the result that all the above studied samples show only diffuse x-ray scattering, i.e. the exhibited scattering patterns consist of amorphous peaks. It is important to note that the x-ray pattern of the bulk polymer PANI (Fig. 3.4.1) and that of the polymer/silica (Fig. 3.4.2 - 3.4.4) seems to be indifferent. This observation clearly indicates that silica particles have no influence on the structure even it incorporated to the matrix. Therefore, the diffraction patterns of the polymer/silica is mostly dominated by the response made by the polymer component. Most of the conducting polymers reported are extremely poorly crystalline [33]. During polymerization, although most of the aniline units are linked through the 1, 4 position, a significant units are couple through other positions. This introduces defects in the hypothetical ideal linear chain arrangment of the polymer and also cause some cross linking of the polymer and consequently results in a significant decrease in the crystallographic order of the chains [35, 36]. As a result, the polymer loses its crystallinity and leads diffuse diffractin pattern as exhibited in the Fig. 3.4.1-3.4.4 Kanazawa *et al* [37] have also reported the amorphous nature of PP as their x-ray analysis revealed no peak in the spectrum.

The observed extremely poor crystallinity may also be related to the doping state of the samples. In fact excellent crystallinity appeared on doping of the conducting polymers has already been reported by various worker [38 - 40]. In those works, the dedoped states of the polymers has been reported as amorphous rich. The present samples have been synthesized chemically and it is well known that chemical synthesized polymers are obtained in their dedoped states. In this respect,

the x-ray patterns observed for the present chemically synthesized samples seems to be reasonable.

3.5 Solid state d.c. conductance and weight change.

Electrical conductivity measurements of the samples PANI, PANI/silica, CH_3-PANI/silica and Cl- PANI/silica were performed by employing conventional two-point probe method. The vacuum dried studied samples were compressed to rigid pellets and stored in a vacuum desiccator till the conductance measurement commence.

The result of the conductivity measurements for the samples is arranged in a bar chart dipicted in Fig. 3.5.1. The electrical conductivity of PANI is usually of the order of 10^{-1} Scm^{-1}, depending somewhat on the polymerization and protonation conditions[41]. The observed conductivity value of the present PANI sample prepared chemically with the $(NH_4)_2$ S_2 O_8 seems to be consistant with the previous findings. The electrical conductance of polymer/silica composites containing almost 40% silica in each sample are also illustrated in the bar chart. The result shows that these composites have significantly lower conductivity than that of the bulk polymer PANI. Presumably this is due to the many additional interparticle contact resistances, present in such finely divided colloidal materials in the solid state. Other group have consistantly reported similar observations for a wide range of polymer and surfactant-stabilized conducting polymer colloids [42-44]. The observed rather lower conductance for CH_3- PANI/silica and Cl-PANI/silica are not understandable in this stage. Since silica content and other synthesis conditions were kept similar to that of PANI/silica samples. The probable factor to influence their conductivity value may be functionality effect.

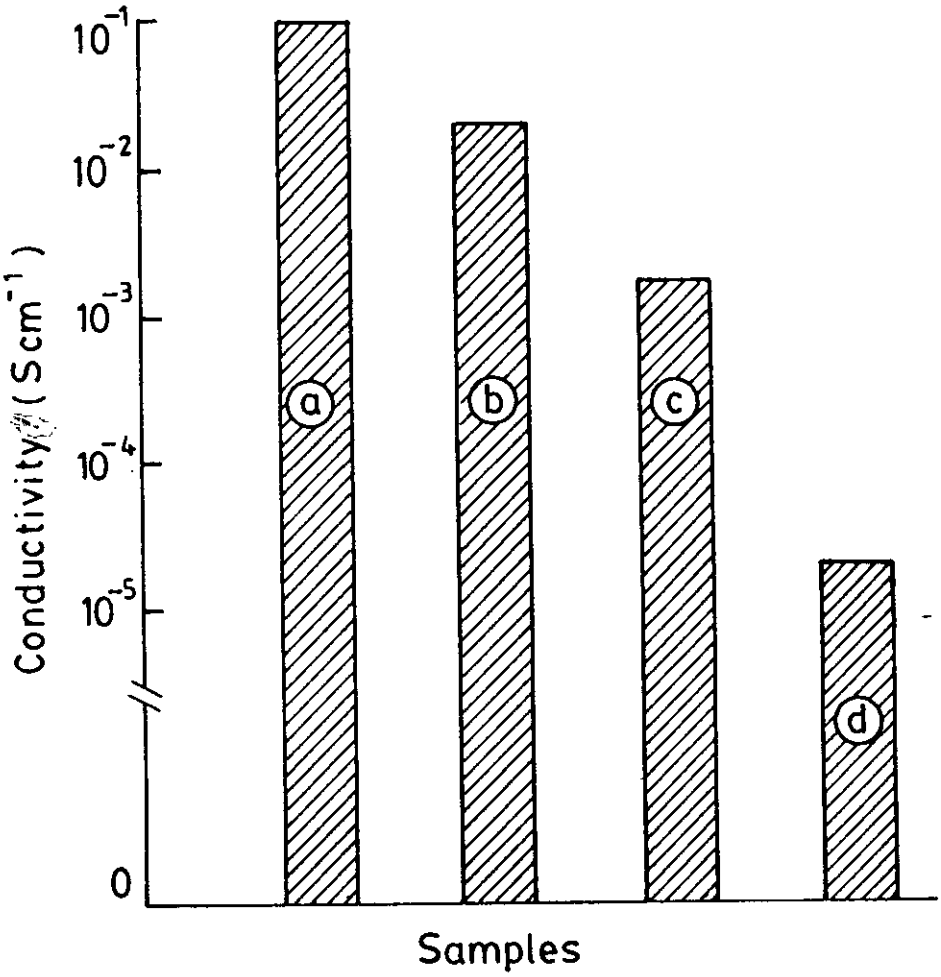


Fig. 3.5.1: Solid state d.c. conductivity of the samples (a) PANI, (b) PANI/ silica (c) CH_3-PANI/silica and (d) Cl-PANI/Silica measured by two point probe method.

Considering this effect, although the result for Cl-PANI is reasonable, the CH_3-PANI sample's conductance is an unexpected one. The lower conductivity obtained with these samples may atleast in part due to the extent of over oxidation of the materials synthesized with the $(NH_4)_2\ S_2O_8$ oxidant [8].

The results depicted in Fig. 3.5.1 also indicate that even the magnitude of conductance of the polymer/silica samples lowered by few order of magnitude relative to the corresponding bulk polymer, their exhibited conductivity values still fall in the range of semiconductor conductivity (10^{-6} to 10^{-1} Scm^{-1}). Since electrical behviour of the composites seem to be controlled by the polymer component, the mechanism of conduction in these composites would be similar to those of the bulk polymer. The conduction mechanism in PANI has been discussed by Li *et al* [45] in terms of the experimentally observed temperature dependence of the charge carrier density. The macroscopic conductivity has been interpreted as a result of anisotropic three-dimensional variable range hopping in a network of rods with metallic behaviour.

Figure 3.5.2 represents the conductivity change of the bulk polymer and polymer/silica samples. After exposing the sample in air, conductivity was measured at different time intervals. The result shows that the conductivities of all the samples decay with time. The magnitude of the decay seem to be different for different samples. However, it can be seen from the results that conductivity change of the samples, in general, is rather faster in the initial several hours. The bulk PANI on exposure to air, its original conductivity lowers very sharply and decreased by more than three order of magnitude. The sample

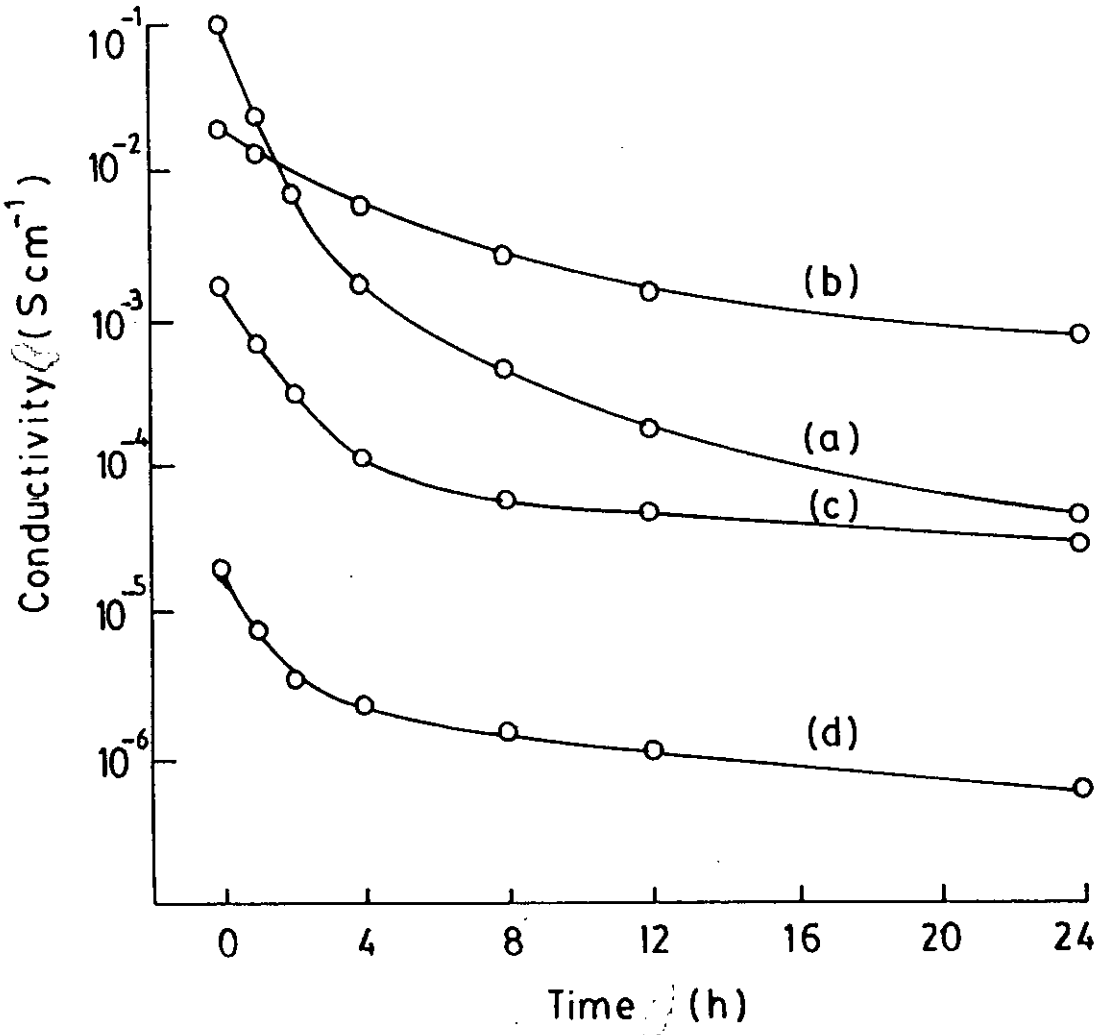


Fig. 3.5.2: Change in conductivity (a) PANI, (b) PANI/silica (c) CH_3-PANI/silica and (d) Cl-PANI/Silica when exposed to air.

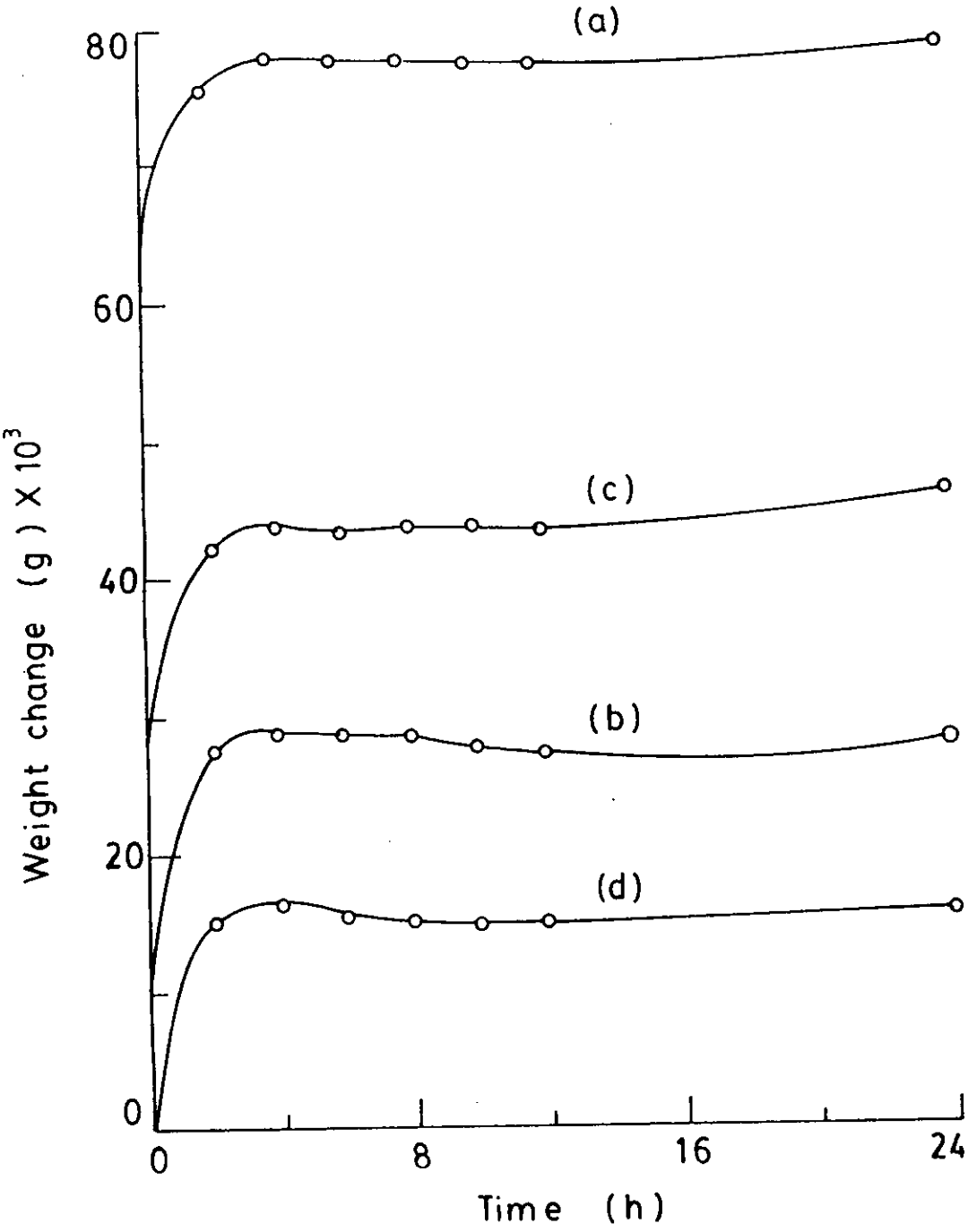


Fig. 3.5.3 (A): Weight change of (a) PANI, (b) PANI/silica (c) CH_3-PANI/silica and (d) Cl-PANI/Silica samples when exposed to air.

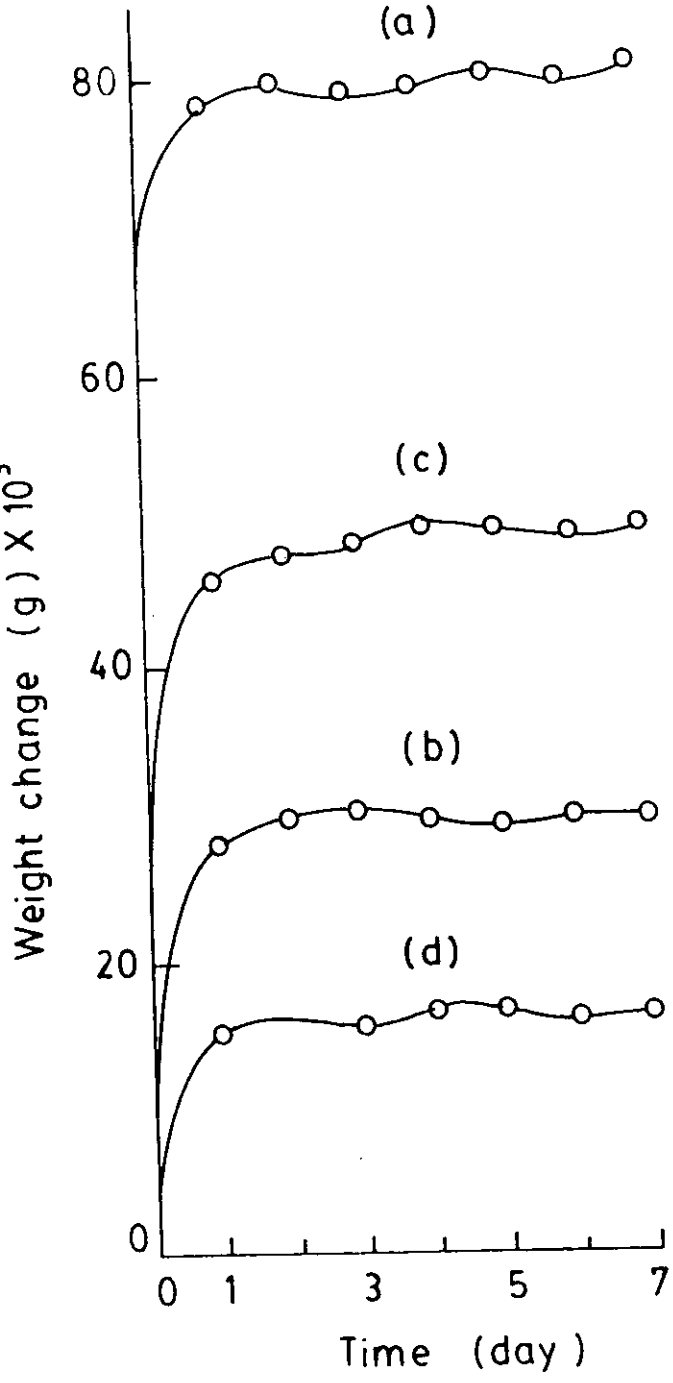


Fig. 3.5.3 (B): Weight change of (a) PANI, (b) PANI/silica (c) CH_3-PANI/silica and (d) Cl-PANI/Silica samples when exposed to air.

PANI/silica, CH_3- PANI/silica and Cl- PANI/silica also affected on exposure to air and shows decay of their electrical properties. However decrease of their conductivity is nearly one order of magnitude which is much smaller than that of PANI. It is interesting to note that the direction and magnitude of the conductivity change for PANI/silica differs appreciably from the other polymer/silica samples as can be seen in Fig. 3.5.2. Evidently, the present findings suggests instability of samples although mechanism for the deactivation of the samples has not been investigated further in the present work. Chowdhury *et. al.* [46] also reported a decrease in the work function and conductivity of doped poly(3-methyl thiophene) film when expose to the air. However, the results would offer better stability than that of its bulk polymer and among the polymer/silica samples studied in this work, PANI/silica exhibits better stability as can be seen from the curve-(b), Fig. 3.5.2.

The effect of ambient atmosphere on the above studied samples were further investigated by measuring weight change when expose them on air. The result is shown in Fig. 3.5.3. The result shows that weight of all the studied samples increase when expose them to ambient atmosphere. The increase in samples' weight may arise from the absorption of moisture. In fact, it has been reported [30] that conducting polymer can absorb water as much as 40% of its mass. The PANI samples (curve-a, Fig. 3.5.3) seems to show the highest affinity for moisture while this affinity appears to be reduced at least to some extent for the polymer/silica samples (curve-b, c and d in Fig. 3.5.3). It is worth mentioning that the samples with the highest affinity for moisture (curve-a, Fig. 3.5.3) show a greater deactivation of the electrical properties (curve- a, Fig. 3.5.2). However, one can see a good co-relation between the deactivation of electrical properties (Fig. 3.5.2) and affinity for moisture absorption (Fig. 3.5.3) of the studied samples. The

deactivation of electrical properties as presented in Fig. 3.5.2 may arise from the absorption of moisture by the samples. On exposure to air, the sample probably absorbed water to cause protonation or even degradation of the polymer by converting imine (= N-) form to amine (-NH-) or any other degraded structures i.e. from a higher conductive states to a lower one. In fact, degradation of PANI in aqueous media has already been reported to be occured via the imine form of PANI which subsequently hydrolysis to form quinone-hydroquinon structures [47].

3.6 Adsorption study

PANI/silica sample prepared chemically was examined by Micromeritrics Sedigraph for its surface area. The observed surface area vs particle diameter exhibited by this sample is shown in Fig. 3.6.1. The result predicts that PANI/silica composite offer a surface area as high as 3.2 m^2/g. The surface area for the bulk PANI was not possible to study in this work. However, Maeda *et al.* [48] reported five times higher BET surface area for PP/silica composites than that of its bulk PP. As with the previous observation, we also expect that incorporation of the silica particles into the polymer matrix would lead an increase of surface area than the bulk polymer. However, the observed surface area for the studied PANI/silica matrix, made us interested to study adsorption process on the sample. For this purpose, adsorption of MB on PANI/silica was examined. Adsorptin was followed spectroscopically by the change in concentration of MB at different time interval Fig. 3.6.2. Detail of the experimentation has been described in section 2.11.

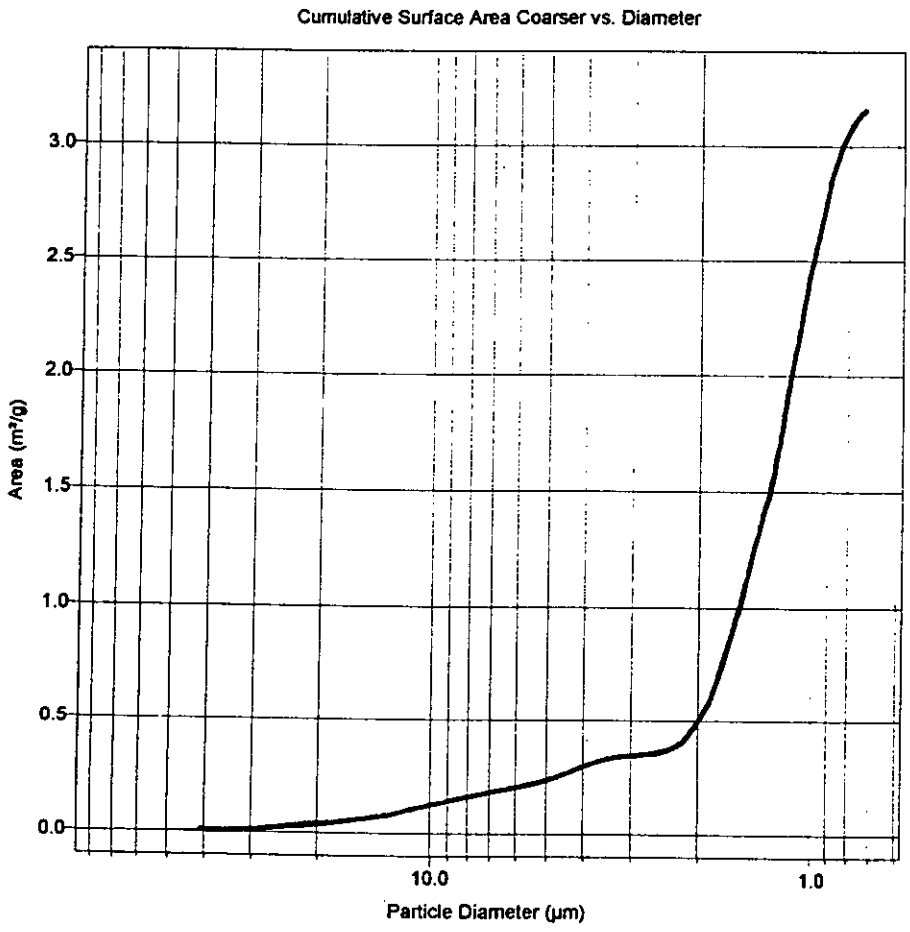


Fig. 3.6.1: Surface area vs particle diameter plot for the chemically synthesized PANI/silica composite

Fig. 3.6.2 shows the change in concentration of MB with time soon after charging it to the adsorbents, bulk PANI (curve -a) and PANI/silica (curve -b). It can be seen from the results that as soon as the MB solution charged to the adsorbent, a decrease in its concentration was observed. The concentration decay is very sharp for the MB- PANI/silica system (curve -b) compared to that of MB-PANI system (curve -a). The decrease of MB concentration appears to be rather faster in the initial few minutes and gradually become nearly unchanged with the lapse of time. This point of saturation may be termed as equilibrium time of adsorption. For PANI/silica system, this point observed nearly at about 120 mins. The decrease in the concentration of MB on charging it to the absorbent, PANI and PANI/silica may be attributed to the adsorption of MB on those matrices. Silica particles have a net negative surface charge under the experimental conditions employed here [8]. Since MB is in the cationic form so adsorption of MB on the PANI/silica is quite likely. However, the adsorption of MB on the bulk PANI is not understandable at present. Similar observation was also reported [18] for the adsorption of nitrongen on bulk PP and PP/silica matrices. The extent of adsorption of MB onto PANI/silica (curve - b) seems to be five times higher than that for bulk PANI (curve -a). This finding may suggests that PANI/silica matrix possesses relatively high surface area. This surface area is nearly five times higher than that of the corresponding bulk PANI. This result seems to be consistant with a previous study involving nitrogen adsorption onto PP and PANI/silica matrix [48]. Most of the conducting polymer/inorganic oxide composites reported to be exhibited considerable porosity. This observation suggests that such composite particles might be interesting new stationary phase substrates for chromatography applications.

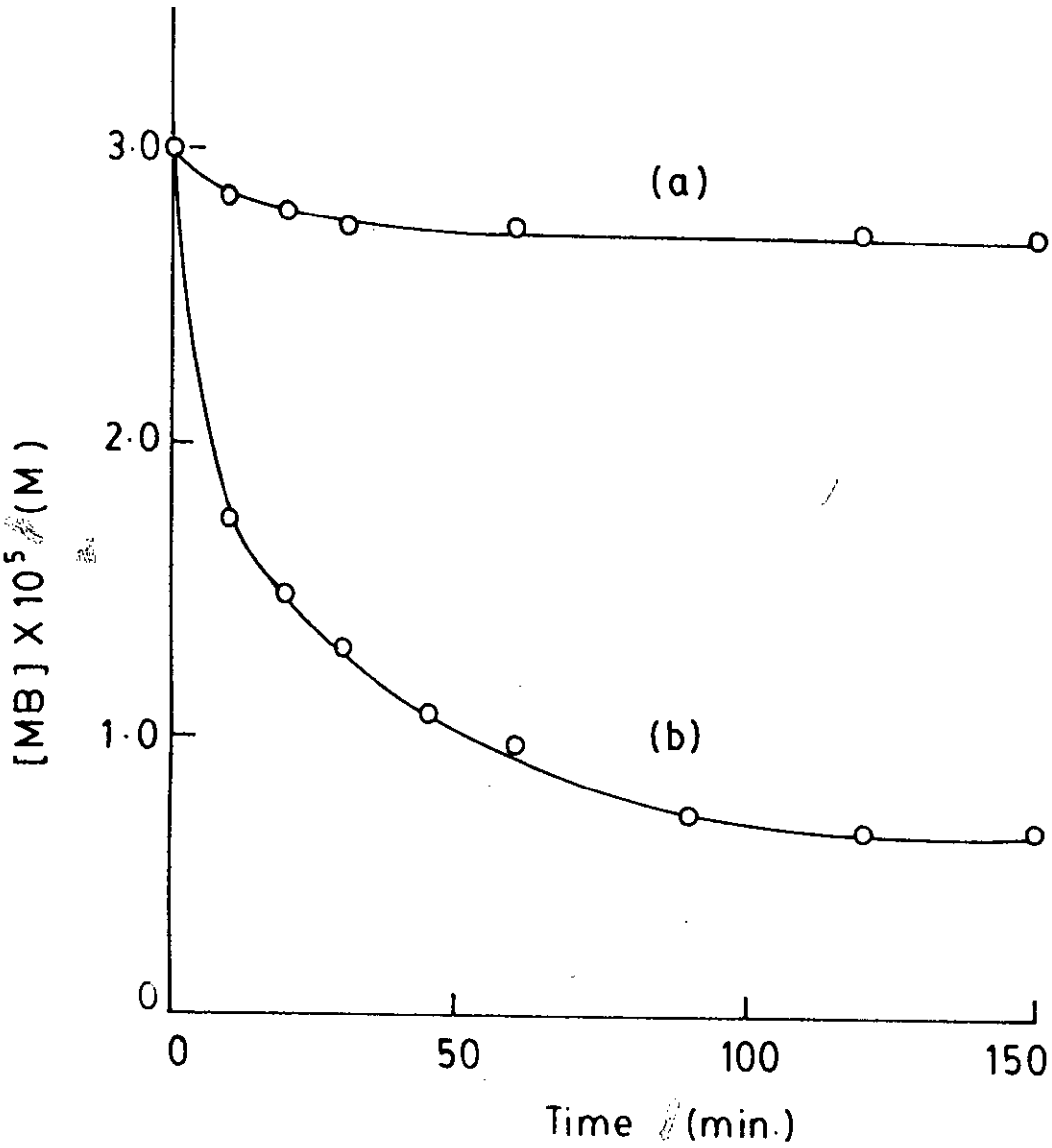


Fig. 3.6.2: Change in [MB] with time on charging on to (a) PANI (b) PANI/silica adsorbents

3.7 Electrochemical synthesis of PANI/silica composite

It is well known that anodic oxidative polymerization is one of the most powerful methods for preparing electroactive polymer films such as PP, PT and PANI. Some of them can be electrochemically oxidized (doped) and reduced (dedoped) reversibly. These observations indicate the possibilities of electrochemical preparation of conducting polymer/silica composites. In fact, Yoneyama's group have incorporated a range of inorganic oxides into electrochemically synthesized thin films of PP and PANI [10-12].

Table 3.7.1 : Silica content and density data for electrochemically synthesized samples.

Name of the sample	Silica content (%)	density (g cm^{-3})
PANI	-	1.42
PANI/silica	28.23	1.53

Cyclic voltammetry is a useful method to investigate the process of the electrochemical polymerization. Figure 3.7.1 shows the CV during the electrochemical synthesis of PANI (a) and PANI/silica composite (b). The CV in 0.5 M aniline/1.0 M HCl and 0.5 M aniline/1.0 M HCl/colloidal silica aqueous solutions, show typical examples for electrosynthesis of PANI and PANI/silica composite, respectively. The anodic peak around 0.93 V vs SCE is assigned to the formation of the radical cations of aniline by electrochemical oxidation. The anodic peak intensity gradually increased with increasing cycle number due to that of PANI films deposited on the electrode[13]. Both the CV seems to be indifferent showing similar electroactive sites in them although the CV in (b) resulted from an electrolytic solution containing colloidal silica. However, it is expected that

colloidal silica may incorporated to the polymer during its electropolymerization. The thus electrosynthesized PANI/silica sample was analysed for its chemical composition (silica content) by hydrofluorization method. The result indicated a silica content of approximately 28% in the electrochemically synthesized PANI/silica matrix (Table 3.7.1). Densities of the samples PANI and PANI/silica synthesized electrochemically were determined by using an auto pycnometer. The results are also shown in the Table 3.7.1. The PANI samples density value has been found to be lower than that of PANI/silica one. However, the observed results of density may support again the silica incorporation into the PANI matrix during its electrosynthesis. The presence of silica in the electrosynthesized PANI/silica composite has also been evidenced by IR analysis of the matrix.

IR spectroscopy studies yielded useful, albeit qualitative information on the electrochemically synthesized PANI/silica composite as can be seen in Fig. 3.7.2. The spectrum of the bare silica control sample as reported by early worker [8] had two major bands at 801 cm^{-1} (scissor deformation) and 1111 cm^{-1} (three superimposed bands due to the Si-O stretch mode). The spectra of the electrochemically synthesized composite (Fig. 3.7.2) exhibited absorption bands attributable to both PANI and silica (813 and 1117 cm^{-1}) components. Band observed in the IR spectrum near 3560 cm^{-1} may indicate water molecule that may absorbed by the polymer [30]. The observed and standard bands assigned for different functional group are summerized in Table 3.7.2.

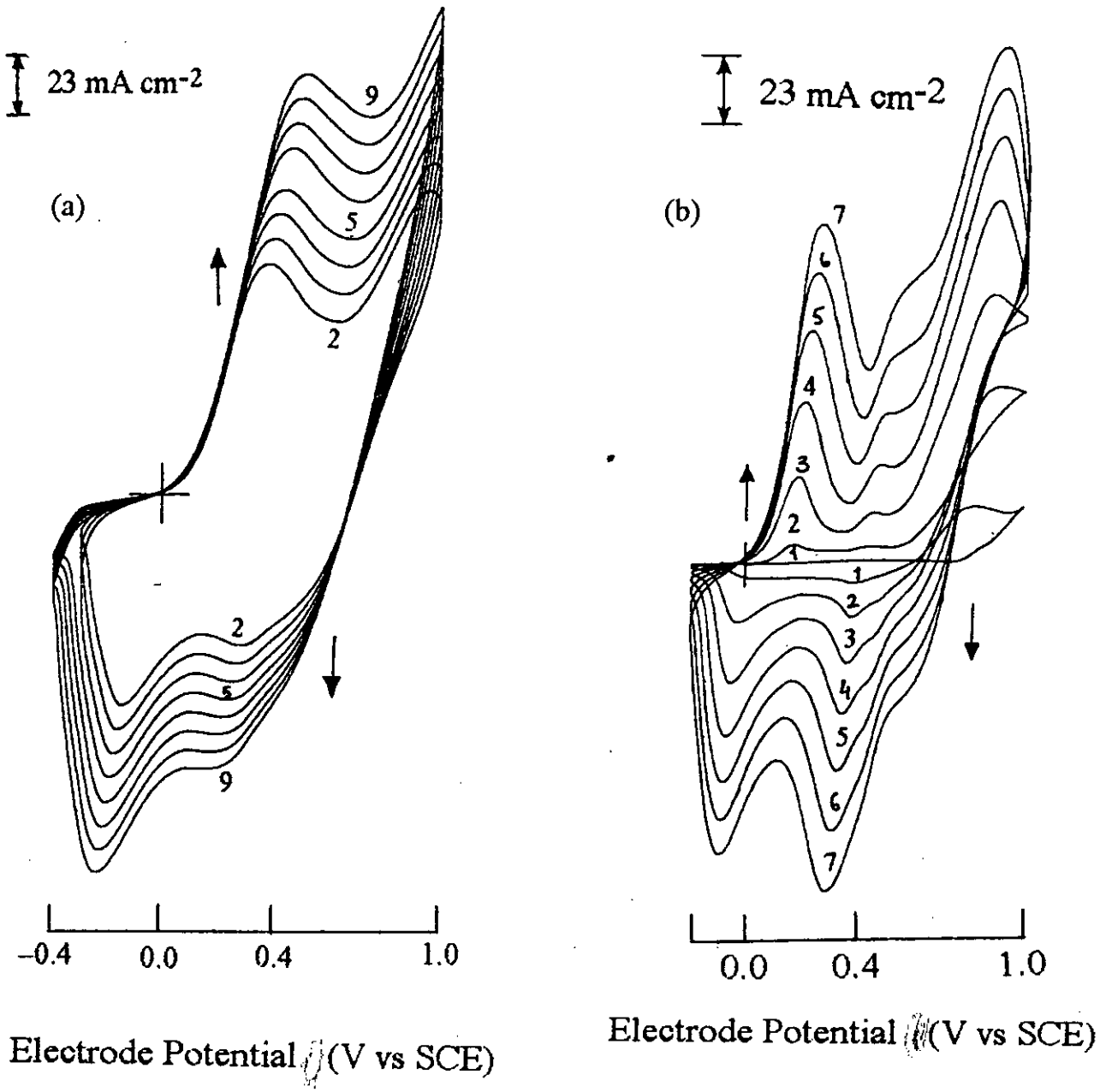


Fig. 3.7.1: CV during electrochemical synthesis of (a) PANI and (b) PANI/silica composite

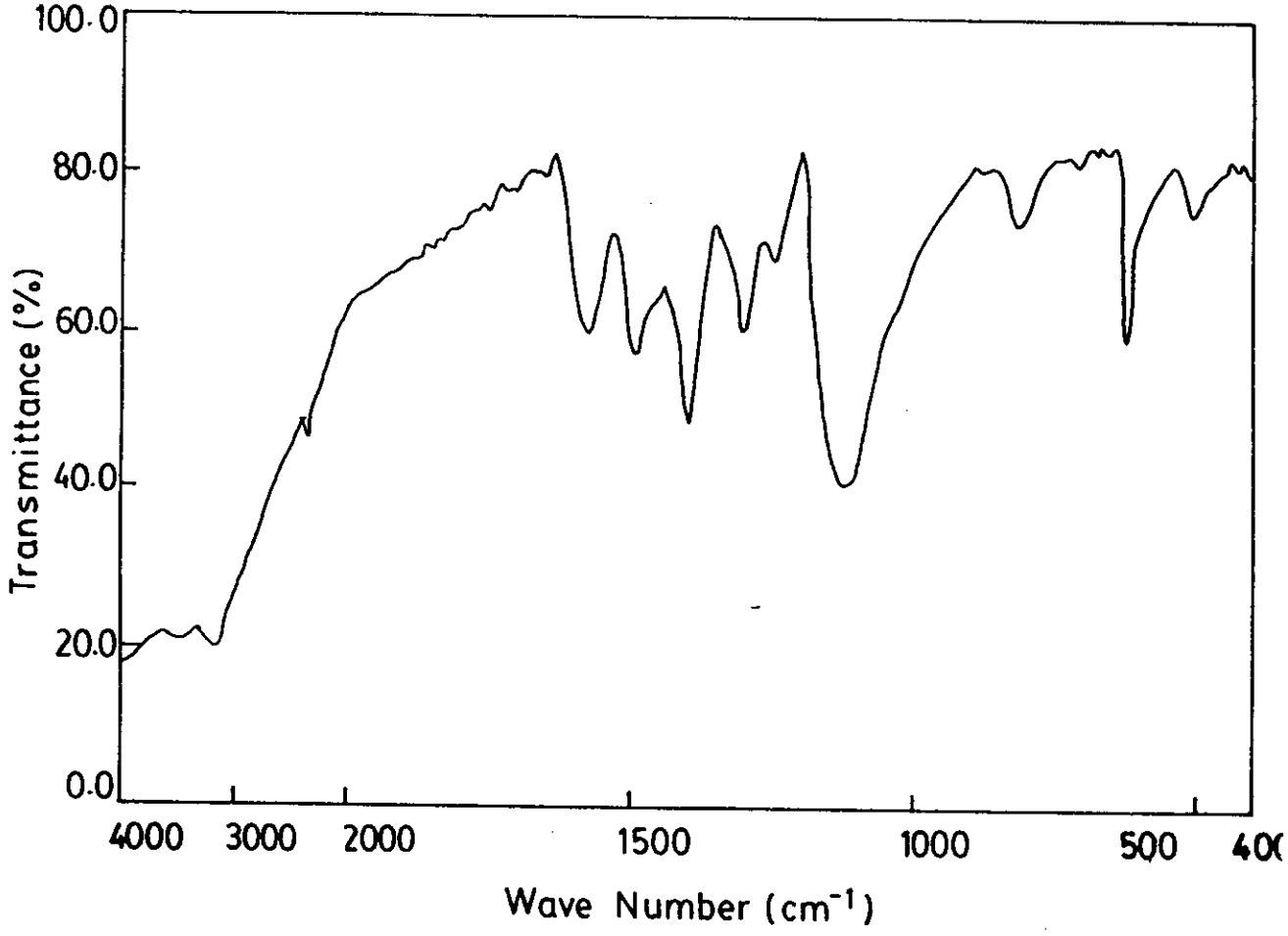


Fig. 3.7.2: IR spectra of PANI/silica composite prepared electrochemically.

Table 3.7.2: Observed and standard IR absorption bands assigned for different functional groups for PANI/silica prepared electrochemically.

Functional groups	Standard absorption band range (cm^{-1})	Observed absorption bands (cm^{-1}) for the sample prepared electrochemically	Probable assignment
Free O-H	3590-3710	3560	O-H stretching vibration water may be present
N-H	3300-3500	3305	Aromatic secondary amine may be present
C=C	1600-1450	1568	C=C stretching in aromatic nuclei
C-N	1350-1250	1296	C-N stretching in aromatic amine
C-H	690-900	875	C-H deformation. Monosubstituted benzene
C=N	1690-1640	1674	=C=N stretching in imine
Si-O	801, 1111	813, 1117	presence of SiO_2

3.8 Doping characteristics

CV is an excellent method to study the electrochemical doping. In Fig. 3.8 CVs are reported for the doping process of electrochemically synthesized (a) PANI and (b) PANI/silica in an aqueous solution containing 1.0 M HCl. Both the CV involved sweeping the potential between -0.2 to 1.0 V vs SCE at a scan rate of 100 mVs^{-1}. The results clearly show that both PANI and PANI/silica films can be switched between their oxidized (conductive) and reduced (insulator) states. It can be seen from the Fig.s that both CV are composed of mainly two redox couples. This behaviour indicates the presence of variable electroactive region both in the PANI and PANI/silica samples. From this results it is quite evident that even after incorporating insulating silica particles into the PANI matrix, it (Fig. 3.8(b)) exhibits excellent electroactivity which is as good as that of the bulk PANI film (Fig. 3.8(a)). During electrochemical oxidation (doping), the anions (Cl^-) in the solution become incorporated into the polymer to compensate the positive charges

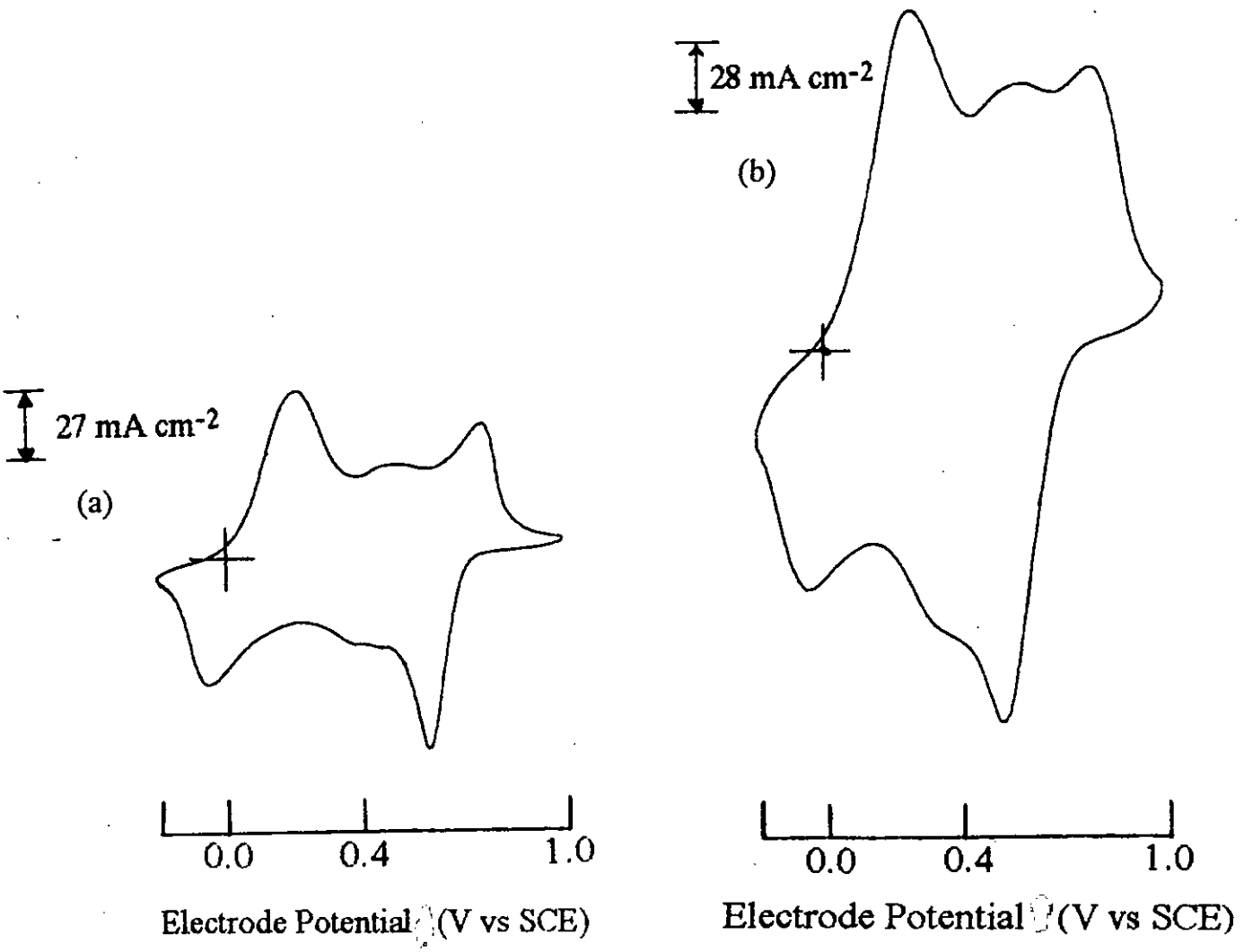


Fig. 3.8: CV of a (a) PANI and (b) PANI/silica films on a Pt electrode in an aqueous solution containing 1.0M HCl. Scan speed: 100mVs^{-1}.

in the chain while in the reduction (dedoping) processes the incorporated anions get removed out of the polymer film [14-15]. In case of PANI, most of the authors proposed that the redox processes appeared in its CV are associated to the protonation as well as to the insertion of anion in the film [16-18]. However, Shacklett *et al.* [19] proposed that the first set of voltammetric peaks correspond to the formation of the radical cation (polaron) and the second set of peaks correspond to the dication (bipolaron). Switching from doped to dedoped states was accompanied by concomitant color change of the polymer. In the present system, doping and dedoping of the Cl^- anion caused a color change of the PANI film. A deep green color was observed in the doped state of both the PANI and PANI/silica films. While a yellowish green color was seen in their dedoped state. Similar observation with PANI samples has also been reported by other workers[13].

3.9 UV-VIS absorption spectral analysis of electrochemically synthesized composite

Figure 3.9.1 shows the UV-VIS absorption spectra of the electrochemically synthesized (a) PANI and (b) PANI/silica composite films diposited on the ITO-coated glass electrode during the electrochemical polymerization. The UV-VIS absorption spectra of both the samples reveals two relatively broad bands : one band centers at about 382 nm and the other intense broad band at about 850 nm, probably results from the interaction between the polymer and the dopant anion (Cl^-), since undoped PANI does not have any appreciable absorption in this region. The broad band near 382nm may corresponds to the interband π-π^* (valence band to conduction band) transition. The results depicted in Fig. 3.9.1 are similar to that reported for thin film of conducting PANI synthesized by electrochemical method

*** PEAK-PICK ***

-- PEAK --		-- VALLEY --	
λ	ABS	λ	ABS
418.0	1.344	578.0	0.520
		254.0	0.047

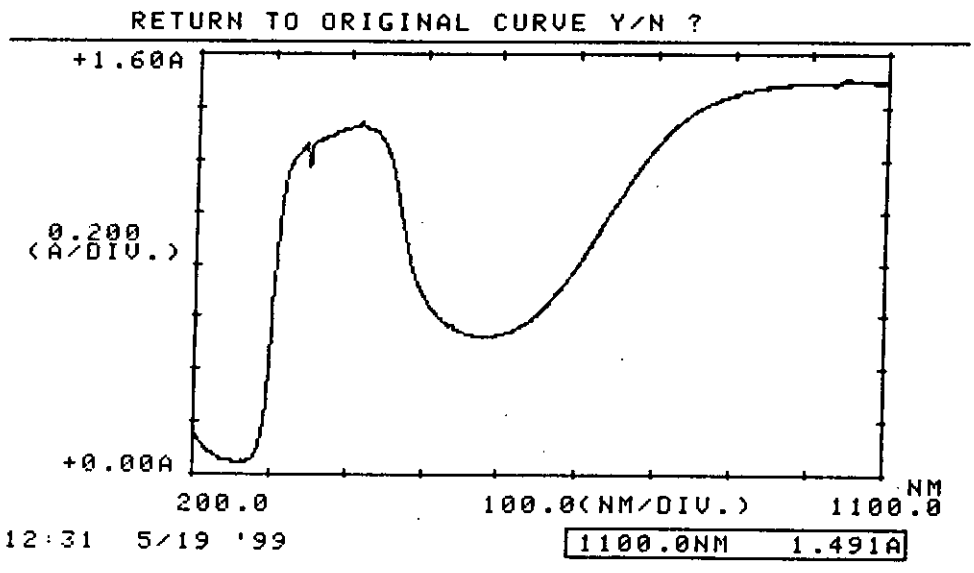


Fig.3.9.1(a): UV-VIS absorption spectra of PANI thin film deposited electrochemically on ITO

*** PEAK-PICK ***

-- PEAK --		-- VALLEY --	
λ	ABS	λ	ABS
847.0	0.564	531.0	0.077
382.0	0.359	277.0	-0.006

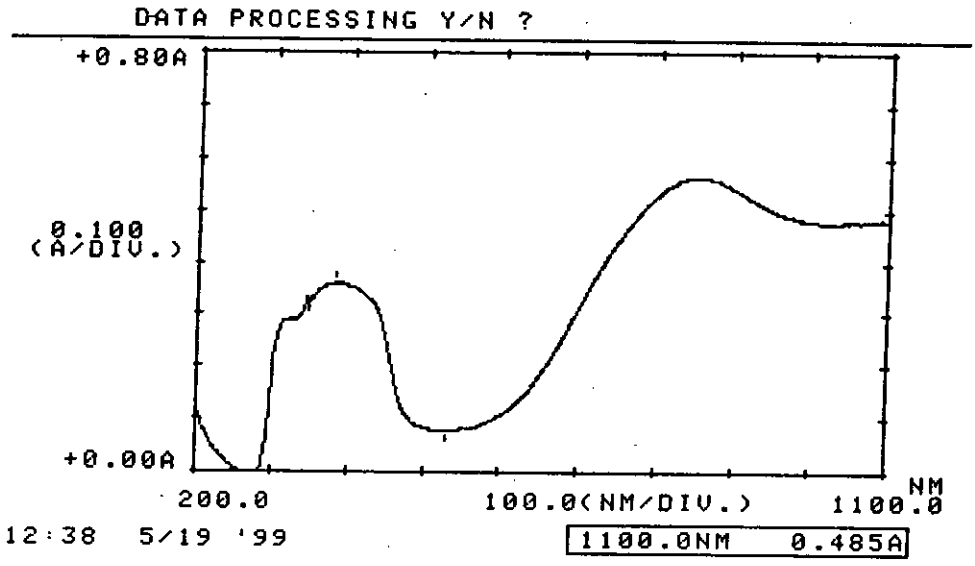


Fig.3.9.1(b): UV-VIS absorption spectra of PANI/silica thin film deposited electrochemically on ITO

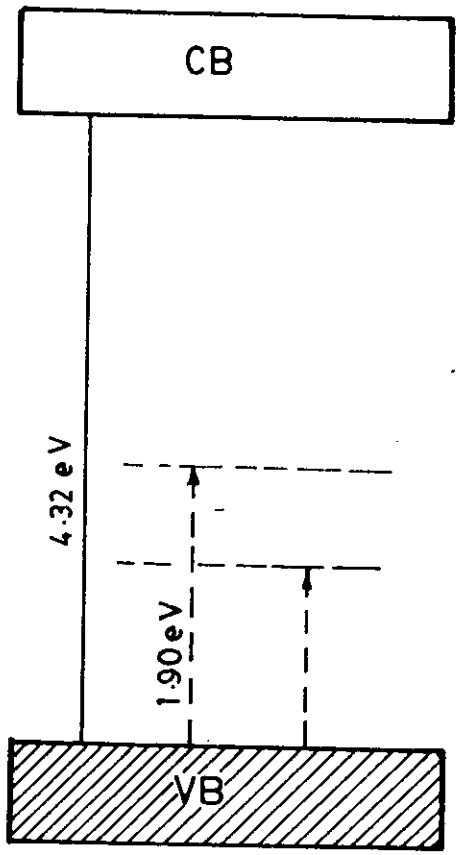


Fig. 3.9.2: Electronic band model of PANI/silica composite based on the optical measurement

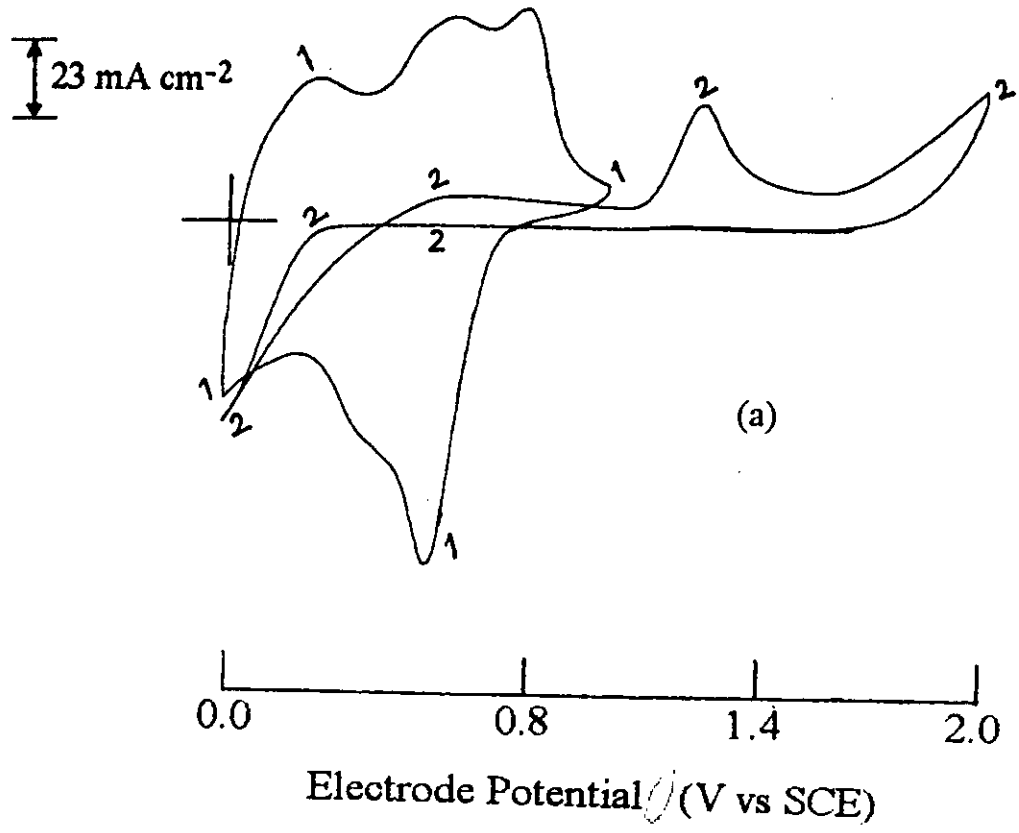
[20]. Thus, the conducting polymer component is present within the PANI/silica composite in its doped conducting state. This observation is consistant with the relatively high solid-state conductivity (up to 0.5×10^{-1} S cm^{-1}) obtained for compressed pellets made from dried powders of these polymer/silica composites (Fig. 3.5.1).

The optical data presented in Fig. 3.9.1(b) provide illucidation of band structure of PANI/silica as drawn in Fig. 3.9.2. The strong absorption band near 382 nm is associated with the interband transition. Therefore, it would represent the band gap of the PANI/silica solid. Within the band gap other transition observed at around 850 nm which may responsible for the composite conductivity by forming polaron and / or bipolaron as mid-gap state. In fact, the formation of polaron and bipolaron have already been evidenced in PANI and other conducting polymer by early workers[21, 22]. However, in constructing the electronic band model of the PANI/silica composite, computation was carried out by considering the peak tails (287 and 650 nm) instead of peak centres (382 and 850 nm) and accordingly band gap has been found to be assigned for this system is 4.32 eV. This result is in good agreement with the previous finding[21].

3.10 Electrochemical degradation

As is well known, electroactive conductive polymers such as PP, PT and PANI can be electrochemically oxidized (doped) and reduced (dedoped) reversibly. However, their stabilities and durabilities in repeated oxidation/reduction cycles have been studied rarely, although some papers [23-25] on their degradation at highly positive potentials, in other words, on the overoxidation, have been reported in recent years. Besides this, to our knowledge, no reports on the electrochemical

degradation of conducting polymer/silica composites have appeared. Fig. 3.10.1 shows the cyclic voltammograms of the (a) PANI and (b) PANI/silica films deposited electrochemically on Pt in aqueous 1.0 M HCl solution. As is well known, the film gave a typical reversible redox response (curve - 1, Fig. 3.10.1a) when the potential scan was reversed at a switching potential of 1.0 V vs SCE. However, when the scan was reversed at a more positive switching potential of 2.0 V, a completely irreversible response without any appreciable anodic and cathodic current was observed (curve-2, Fig. 3.10.1a) or in other words, the electroactive nature indicated by redox peaks in curve-1, Fig. 3.10.1, seems to be destroyed. This phenomenon is called overoxidative degradation and is found in some kinds of conducting polymers as described before. The similar study was carried out with PANI/silica composite and the result is depicted in Fig. 3.10.1(b). The redox peaks as observed in the curve-1, Fig. 3.10.1(b), have found not to be destroyed totally even after reversed the scan at a more positive switching potential of 2.0V (curve-2, Fig. 3.10.1b). It seems from the result that although overoxidation takes place with PANI/silica sample, the extent of degradation is not as drastic as happened with PANI. The result also suggests that even incorporating insultating silica particles in the polymer matrix, it (PANI/silica) still exhibits electroactive nature as good as the parent conducting polymer (PANI) do. Over oxidative degradation may be rationalized as due to the formation of dications of aniline moities in the PANI film. The dications should be very strong electrophiles and easily undergo nucleophilic attack with successive decomposition as shown in Scheme-3.10 [25].



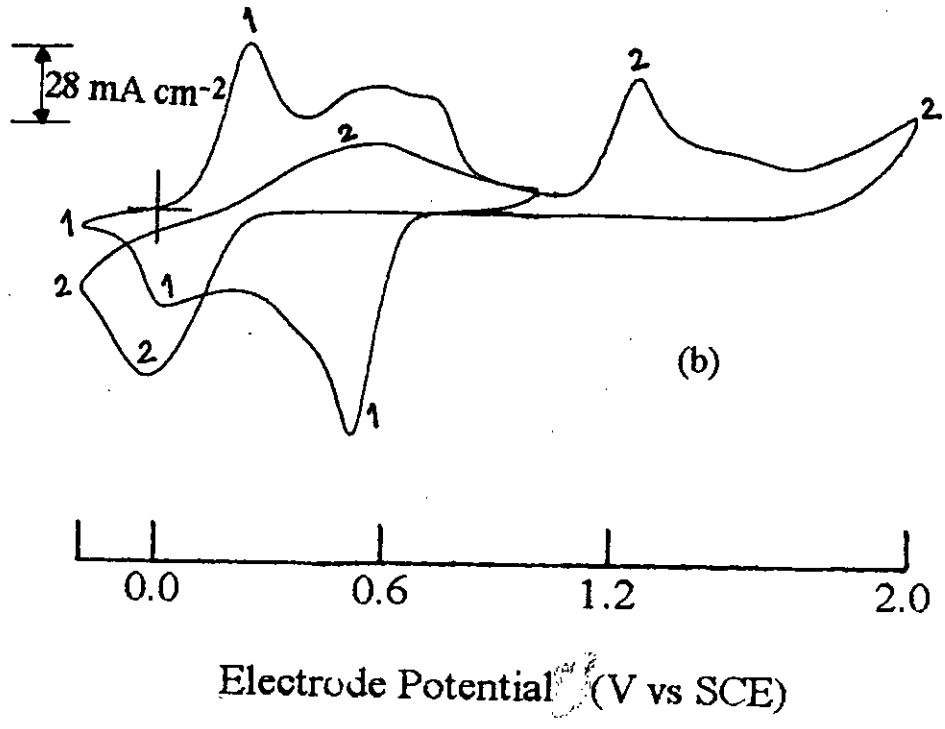


Fig. 3.10.1: CV of (a) PANI and (b) PANI/silica films in 1.0M aqueous HCl solution. :+1.0V (curve -1) and +2.0V (curve-2)

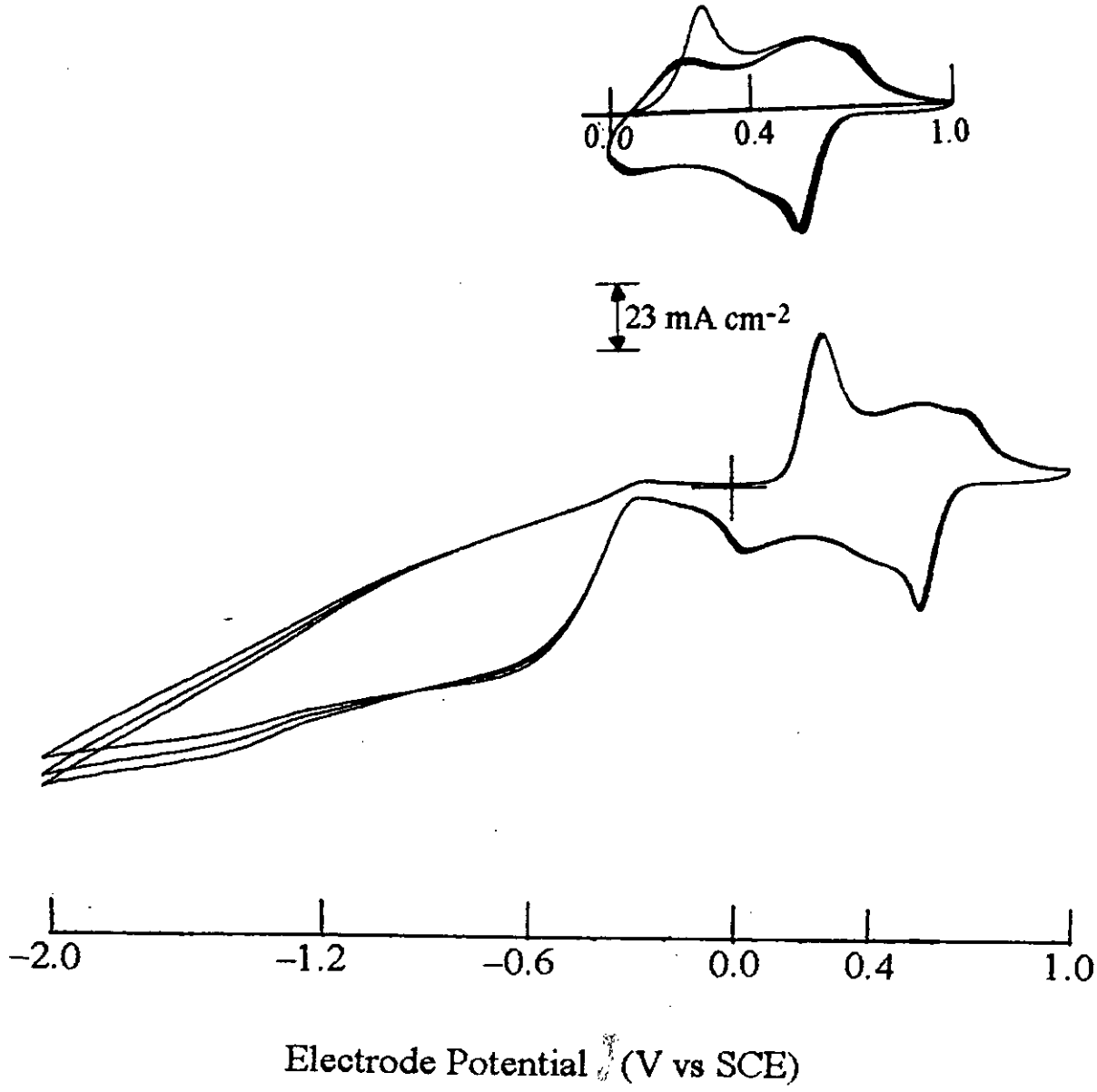


Fig. 3.10.2(a): CV of PANI film in 1.0M aqueous HCl solution. Switching potential: -2.0V.

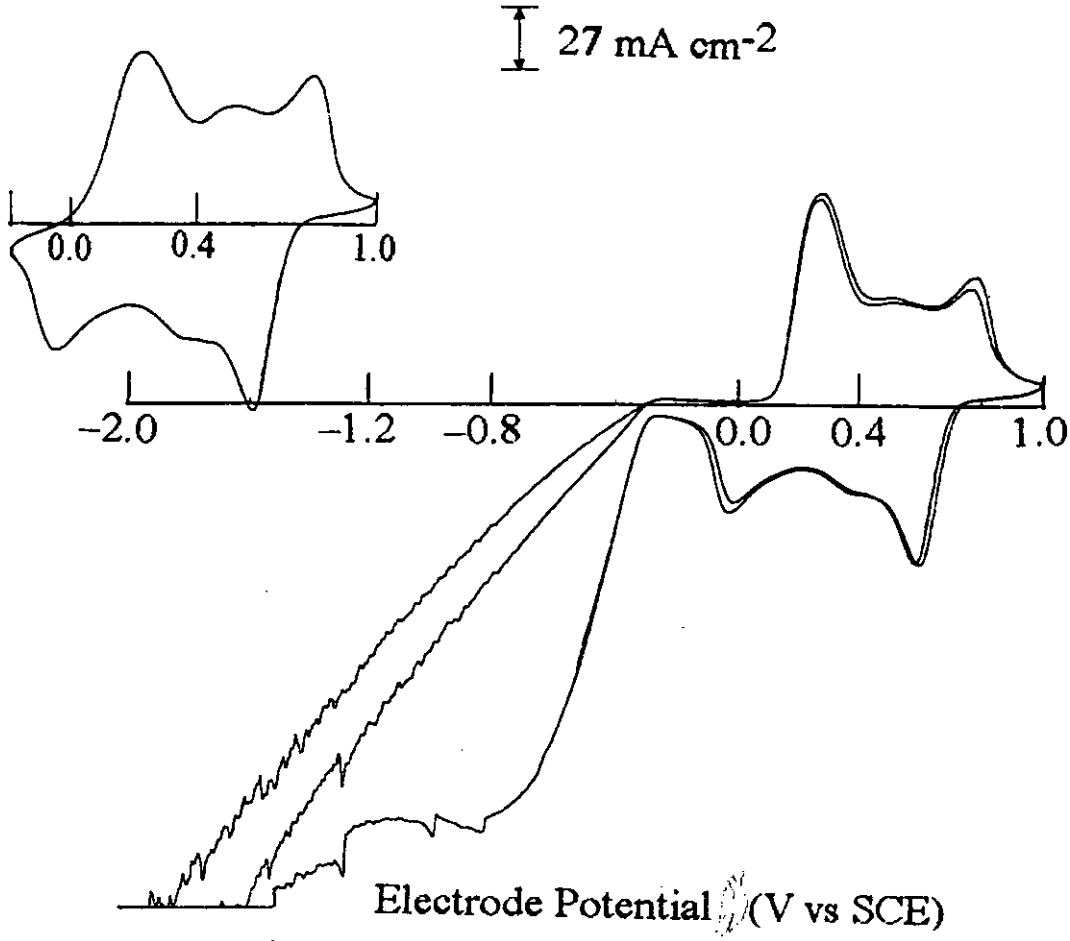
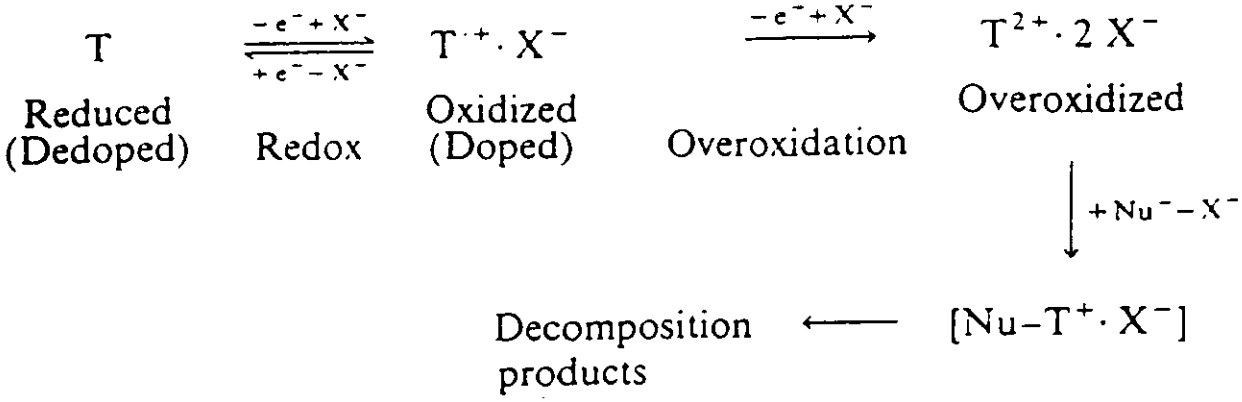


Fig. 3.10.2(b): CV of PANI/silica film in 1.0M aqueous HCl solution. Switching potential: -2.0V.



Scheme 3.10. Overoxidative degradation. T: monomer unit of polymer; X^- : supporting electrolyte anion; Nu^- : nucleophile.

It is interesing to note that no degradation was observed for the samples PANI (Fig. 3.10.2a) and PANI/silica (Fig. 3.10.2b) when the potential scan was reversed at a negative switching potential of -2.0V vs SCE. The results indicate superior stability and durability of the PANI and PANI/silica matrices toward electrochemical cathodic treatment upto -2.0V vs SEC.

In this work, another interesting phenomenon was found, that is a positive shift of the first anodic peak. As shown typically in Fig. 3.10.3, the shift was observed by repeating the scan in 1.0 M aqueous HCl solution. The first anodic peak shifted but the corresponding first cathodic peak did not. Similarly, the scond anodic peak did not shift while the corresponding second cathodic peak shifted. As a result, the

reversibility of the voltammogram was lowered by repeating the scan. This phenomenon is herein called "deactivation" distinguishing it from the degradation [25]. Both the samples PANI and PANI/silica underwent this sorts of deactivation as can be seen in Fig. 3.10.3(a) and 3.10.3(b), respectively. However, the above fact suggests that the deactivation damages the film less than the degradation, i.e. redox response of the films after deactivation (Fig. 3.10.3) is better than that of the films after overoxidation (Fig. 3.10.1).

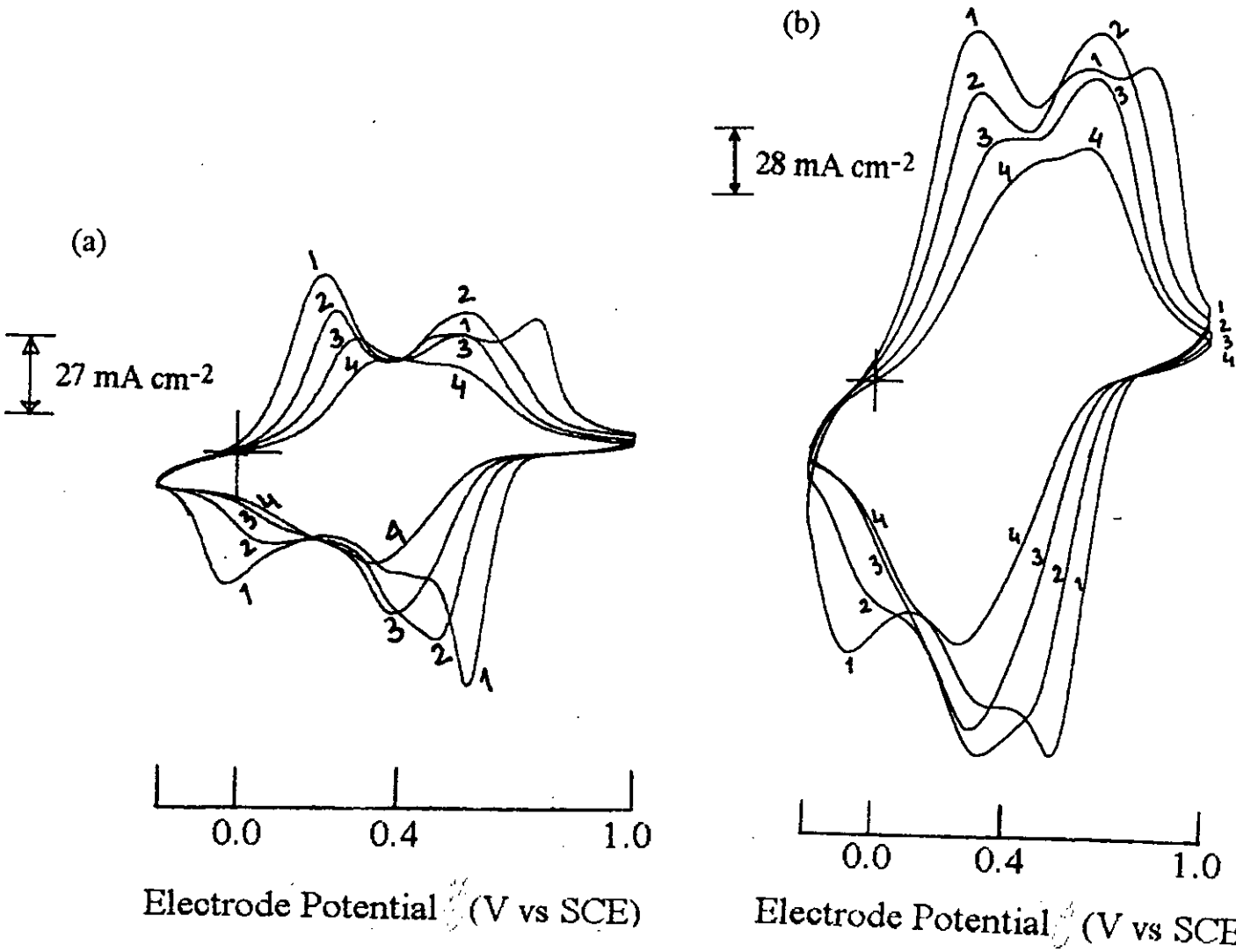


Fig. 3.10.3: CV of (a) PANI and (b) PANI/silica films in 1.0M aqueous HCl solution at different no. of scan cycle:(1) 1st (2) 25th, (3) 75th and (4) 150th.

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Conclusion

The polymerization of aniline, *o*-toluidine and 2-chloroaniline in the presence of colloidal silica represents a novel and facile route for the preparation of conducting polymer/silica colloidal dispersion which utilizes commercially available small silica particles as dispersants. This polymer/silica composites represent a potentially useful processible form of poly(aniline) and its derivatives, normally intractable conducting polymer.

Optical microscopy studies confirm that the polymer/silica composites are made up of microaggregates of the original small silica particles. Under appropriate reaction conditions the silica content in the composites can be as high as 40% by weight. Since silica is incorporated into the polymers, the densities of the composites are significantly higher than the corresponding bulk polymers. Weight-average particle size distribution of the studied composites can be varied depending on the monomer used in the synthesis. In some cases, they can have a reasonably narrow particle-size distribution and may therefore be of interest as "model" colloids.

The solid state compressed pellet conductivities of the polymer/silica composites are lowered by at least an order of magnitude relative to bulk polymer prepared under the same condition. However, still their electrical conductance fall in the range of a semiconductor, i.e. their semiconducting nature remains even after incorporating the insulating silica in their matrix. As evidenced from the XRD studies, the structure of the bulk polymer and the polymer/silica seems to be indifferent i.e. silica can not modify the structure of the bulk polymer which is mostly amorphous in nature. Band model illucidated from the UV-VIS studies of

PANI/silica, assigned a band-gap of 4.32 eV for this composite. This value is very close to the band-gap of bulk PANI. However, the degradation of the electrical properties of the polymer/silica composites by the absorption of moisture is less drastic compare to that for bulk polymer. Our adsorption studies indicate that the synthesized conducting polymer based-composites possesses relatively high surface areas. This surface area is upto five times higher than that of the corresponding conducting polymer synthesized under the similar conditions.

Poly(aniline)/silica composites have also been successfully synthesized electrochemically from an aqueous solution containing colloidal dispersion of silica, monomer and electrolytes. The thus electrosynthesized composites contains 28% silica by weight. This polymer/silica electrodes shows very good electroactive nature relative to the bulk conducting polymer. The electrochemical degradation of the poly(aniline)/silica electrode seems to be lower than that of the bulk poly(aniline) electrode. Hence it may be conclude that even after incorporating insulating silica particles to the bulk conducting polymer, it still exhibits very prominent electroactive characteristics with better electrochemical and environmental stability.

List of Symbols and Abbreviations

Symbols / Abbreviation	Explanation
CV	Cyclic voltammogram
PP	Poly (pyrrole)
PANI	Poly (aniline)
IR	Infra-red
UV-VIS	Ultra violet-visible
XRD	X-Ray diffraction
PT	Poly (thiophene)
SCE	Saturated calomel electrode
ITO	Indium-tin oxide
s	Second
h	Hour
V	Volt
min	Minute
S	Siemen
A	Ampere
cm	Centimeter
CH_3-PANI	Poly (*o*-toluidire)
Cl-PANI	Poly (2-chloro aniline)

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