CHAPTER – I

GENERAL INTRODUCTION

1.1 Introduction

Although every engineering material has a field of application in its pure form, many examples exist in which pure components are mixed to give new materials with tailored properties. One such class of materials is conducting polymer composites consisting of electrical conductive particles incorporated in the insulating matrix of polymers. The first reinforced polymer based materials, used by the people of Babylonia and Mesopotamia around 3000 B.C. find mention in the Holy Bible. These materials consisted of bitumen-based pitch for building products and bundles of papyrus reed in a bitumen matrix for manufacturing boats [1]. The Hindu Vedas (written about 1000 B.C.) refer to the use of lac, a polymer material composed of polyether and polyester chains, with fine sand for the production of whetstones (a shaped stone used for sharpening tools), which were known in India and China for several thousand years. In Mahabharata also lac was reportedly used by the Kauravas to make a palace to wipe out Pandavas deceitfully. The research in the field of polymeric materials is as old as the inception of life and there are innumerable examples that could date back the origin of polymer composites into antiquity [1-3], but science of enhancing and modifying the properties of polymer materials by adding suitable fillers has been practised extensively not earlier than last century.
The modern industry demands advanced materials and products engineered to have special properties that guarantee performance in certain applications. There is a demand for modified polymers and plastics with various structures and properties tailored not only to meet high performance criterion, but also to 'delight' customers by providing new and unexpected advantages. The vigorous development of polymer science and the extensive utilization of polymeric materials in their pristine or mixed/modified form in technology has led to the increased interest to various problems of physics of polymers in recent years. The study of polymeric composites is highly important for the understanding of many scientific and practical problems associated with the use of these materials in modern engineering. This accounts for the fact that not only physicists but also synthetical chemists, technologists and structural engineers have become more and more interested in the field of polymer composites. To associate various theories and models prevailing at present, with the properties of the polymer composites that are encountered during their experimentation, is indeed a difficult task because the science of these materials is rapidly progressing and many principles are becoming outdated and being replaced by new ones, which are often still not completely proven and authentically tested.

1.2 Polymers; definition and basic concepts

Although the aim of the present study is fabrication of polymer composites by adding conducting fillers in electrically non-conducting polymers and characterization of these composites for exploring the possibility of using them as current and temperature sensors, a basic understanding of general properties of polymers [4] is essential.
Polymers are substances whose molecules are composed of a large number of repeating groups, called monomer units (the group at the ends of the molecule i.e. end groups, differ to some extent in structure from the principal monomer units, or chain units). The number of monomer units in a molecule is called the degree of polymerization, generally denoted by the letter n. The value of n may vary from a few units to few thousand or even more. Polymers with a high degree of polymerization are called high polymers while those with a low value of n are known as oligomers. The name of the polymer is usually derived from the name of the monomer by adding to it the prefix poly e.g. polystyrene, polyethylene, and polyvinylchloride.

Polymers are classified as linear, branched and three-dimensional or cross-linked. Linear polymers are substances composed of linear molecules, i.e. molecules in which each monomer unit, with the exception of the end groups, is linked only to the two adjacent monomer units. Linear molecules are also called polymer chains. A branched polymer is a long chain with side branches, the number and length of which may vary widely. There are practically no strictly linear polymer molecules. More or less all are branched to some degree. Polymers composed of molecules linked together by chemical bonds (cross bonds), so that a three-dimensional space network is formed, are said to be three-dimensional. Polymers that form three-dimensional networks are commonly known as thermohardening polymers or thermosets. Thermosets are made from basic products in a state of partial polymerization. In the mold, when the material is already formed, full polymerization is achieved by the action of catalysts, accelerators and heat. A thermoset forms crosslinks when it gets hot. These crosslinks are like glue that hold the polymer chains together. So, with heat, crosslinks form, and the polymer gets harder and it is called "curing" the polymer. After being fully cured, the thermoset form is irreversible.
Polymers in which no chemical cross links form on heating and which become soft at a certain temperature are called thermomelting or thermoplastic polymers. Thus thermoplasts get soft when they get hot and get hard when they cool. Almost 85% of polymers produced worldwide are thermoplastics. Over 70% of the total production of thermoplastics is accounted for by the large volume, low cost resins e.g. polyethylenes (PE) of different densities, polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC). Next in performance and cost are acrylics, acrylonitrile-butadiene-styrene (ABS) and high-impact polystyrene (HIPS).

Polymers consisting of identical monomer units are called homopolymers. Polymeric compounds containing several (usually two) types of monomeric units in their chain are known as copolymers or mixed polymers. Copolymers may also be linear, branched or crosslinked. In copolymer molecules the monomer residues may be arranged in the chain at random, according to the laws of probability, or regularly. Copolymers of the former group are called irregular and those of the latter 'regular'.

Polymers are also classified in accordance with the regularity with which the side groups are arranged with respect to the main chain. If the polymer chain is conceived to be stretched out in a straight line, the side groups will be arranged either on one side of the chain or they will alternate regularly or they will alternate at random (isotactic, syndiotactic and atactic polymers respectively).

1.2.1 Phase States and Phase transitions

To get a clear idea of the phase state of matter it is necessary to consider the phase concept. The term phase can be defined structurally and thermodynamically. In thermodynamics, a phase is defined as part of a system separated from other parts by interfaces and differing from them in thermodynamical properties. A phase must possess sufficient extent (volume) for the concepts of pressure, temperature and other...
thermodynamic properties of the phase to make sense. Phases should be separable from one another. From the structural standpoint phases differ in the order of mutual arrangement of their molecules. Depending on this order one distinguishes between three phase states, namely: solid, liquid and gaseous. The solids in turn may exist in two forms or phases viz. crystalline and amorphous (or glassy) phases. The crystalline phase state is characterized by a three-dimensional long-range order in arrangement of atoms or molecules. Long range order is an order observed over distances hundreds and thousand of times greater than the size of the molecules, and may exist in one two or three dimensions. Long-range order in one dimension is that of an ideal molecular chain of a polymer in which the same unit is repeated regularly. Crystals are structures having long-range order in three dimensions.

The amorphous phase state is characterized by absence of a crystalline lattice and it is often called amorphous. In this state the packing of molecules or atoms is approximately the same as in the crystalline state. Since the molecules or atoms are adjacent to one another, the random arrangement is impossible. The amorphous state has short-range order, i.e. an order that is observed over distances commensurable with molecular size. In the vicinity of any given molecule its neighbours may be in a definite order, but at a small distance from the molecule this order no longer exists.

The liquid phase is the state of substances at temperatures above their melting points and of all solid amorphous substances (e.g. ordinary silicate glass). Since silicate glass has no crystalline lattice, all solid amorphous bodies are said to be glassy or glasses. Glassy and crystalline bodies are both in the solid aggregation state and do not differ in mobility and packing of their molecules. It thus follows from the above discussion that two-phase states may correspond to the solid physical state namely crystalline and glassy.
Phase transitions are transitions from one phase to another, i.e. transitions involving a change in mutual arrangement of molecules and in thermodynamic properties of the substance. Phase transitions may be of first and second order. First order transitions are accompanied by a discontinuous change of internal energy and specific volume. These transitions involve absorption or generation of heat e.g. melting, vaporization and sublimation etc. In second order transitions the internal energy and specific volume change smoothly i.e. no heat is evolved or absorbed.

1.2.2 Crystallization and Glass transition

There are inherently two possible ways of passing from the equilibrium liquid state into the solid state, namely, crystallization and glass transition. Crystallization is the transition from a state of short-range order to one of long-range order, i.e., the process of formation of a new phase. It is, therefore, a phase transition. Glass transition is the passage of a mobile liquid into the solid state with retention of short-range order and absence of long range order; hence, glass transition is not a phase transition [4]. Crystallization occurs at a strictly definite temperature (crystallization or melting point), below which the equilibrium state is the crystalline state, because the thermodynamic potential of the crystal is smaller than that of the liquid.

However, at temperatures below the crystallization point the same substance can also be obtained in the so-called supercooled state (by supercooling the melt). A supercooled liquid is always in a nonequilibrium state, and sometimes insignificant changes in external conditions will cause crystallization. When a liquid is cooled at a sufficiently fast rate (and especially if it is supercooled), its coefficient of viscosity increases and its energy of thermal motion decreases ($E = kT$). This prevents the molecule from regrouping to form a crystalline lattice. At a certain temperature the coefficient of viscosity of the liquid approaches $10^{13}$ poises, which corresponds to the
viscosity coefficient of a solid. The super-cooled liquid solidifies, but no crystalline lattice is formed, and the substance passes into the glassy state, i.e., becomes glassy or vitreous. The temperature at which the viscosity of the amorphous substance becomes equal to $10^{13}$ poises is called the glass-transition temperature, or glass point, $T_g$. When a substance assumes a glassy state, all its properties change: it loses properties characteristic of the liquid state and acquires the properties of a solid. These changes do not occur jump wise, but gradually, over a certain temperature interval of about 10 or 20°C. Therefore, the glass transition temperature is not a point, but the average of this interval.

1.2.3 Crystalline and Amorphous polymers

An important feature of crystalline polymers is that they consist not only of crystalline but amorphous regions as well. It is necessary to remember that the concept of the structure of a crystalline polymer as an assembly of distinct phases as an idealization. As a matter of fact, portions with an intermediate degree of ordering separate the crystalline and amorphous regions. As a rule, there is no sharp borderline between the crystalline and amorphous regions. This is associated not to a small degree with the fact that a macromolecule may run through several crystallites and amorphous regions. The existence of such two-phase chains is a characteristic feature of crystalline polymers. It is exactly such chains that are eventually responsible for the strength of polymers; they are taking the main part of loading stress upon deformation of the polymer. It is sometimes believed that a crystalline polymer may be regarded as an amorphous matrix in which small crystallites are randomly distributed.

Many polymers incapable of crystallization are in an amorphous state. Owing to the slow kinetics of the crystallization process, crystallizable polymers may supercool and likewise pass over to an amorphous state, which is consequently a very
common state for polymers. Depending on temperature, amorphous linear polymers may be in three physical states: glassy, rubber-like, and viscofluid.

The glassy state is characterized by vibrational motion of the atoms constituting the chain about an equilibrium position. There is practically no vibrational motion of units or movement of the chain as an integral whole. The rubber-like state is characterized by vibrational motion of units (torsional vibrations); as a result of which the polymer chain becomes flexible. The viscofluid state is characterized by mobility of the entire macromolecule as a whole.

When a polymer is heated, its units acquire vibratory motion first, the chains beginning to move only at a higher temperature. Hence, with rising temperature an amorphous linear polymer passes from the glassy to the rubber-like, and then to the viscofluid state. On lowering of the temperature the polymer passes through all three states in the reverse order.

Transition of a polymer from one state of aggregation to another does not occur at any definite temperature, but within a certain temperature range; this is accompanied by a gradual change in its thermodynamic properties. The average temperatures of transition regions are called transition temperatures. The temperatures of transition from the glassy to the rubber-like state (and vice versa) is the glass or glass-transition temperature \( T_{g} \); the temperature of transition from the rubber-like to the viscofluid state (and vice versa) is the flow temperature \( T_{f} \).

1.3 Conducting Polymers

Polymers, or plastics as they are usually called, are long chain molecules made of carbon atoms. Many polymers e.g. polyethene, poly vinyal chloride and
polystyrene find their use in our daily lives. Generally polymers are good electrical insulators ($<10^{-12} \Omega^{-1} \text{cm}^{-1}$). In fact one of the most common uses of polymers is as insulation for electric wires. However under certain circumstances polymer can be made to behave like metals ($>10^{-1} \Omega^{-1} \text{cm}^{-1}$) and such polymers are called conducting polymers.

1.3.1 Types of conducting polymer

The two types of conducting polymer are:

1.3.1.1 Electrconducting Conjugated polymer

Electrconducting conjugated polymers (ECPs) exhibit intrinsic conductivity [5(a)]. Their structure contains a one-dimensional organic backbone based on the alternation of single and double bonds, which enables a superorbital to be formed for electronic conduction. Polyacetylene, polyaromatic and polyheterocyclic chains can provide such a structure. Macroscopic conduction through these polymers takes place by charge hopping both along the polymer chains and also between the macromolecules that make up individual fibers and between the fibers themselves. In the undoped state, however, these materials are only semiconducting. Conjugated polymers e.g. polythiophene and polyanilene, which contain many double bonds in their structure, are actually semiconductors with unusual electrical properties. Conjugated polymers have been studied with the idea that $\pi$ electrons that are delocalized along the chains of these polymers could give conductive properties to these systems similar to those of semiconductors. The first conductive polymer thus realized after successful doping was polyacetylene. Since this discovery many conductive polymers have been developed from several monomers that produce conjugated systems after polymerization. Conductive polymers are mainly
synthesized by chemical or electrochemical oxidation of monomers in solutions containing a supporting electrolyte.

The electronic conductivity appears only when the material is doped, i.e. when electrons or holes are injected into the superorbital. For reasons of electroneutrality, counter ions called dopants are simultaneously inserted into the polymer matrix. They are generally synthesized by electrochemical polymerization [5(b)].

In year 2000 the Nobel Prize for Chemistry was awarded to Alan Heeger, Alan MacDiarmid and Hideki Shirakawa for the discovery of electrically conducting polymers. They discovered that by adding bromine to polyacetylene, its conductivity could be increased by a factor of ten million [6]. This technique is called chemical doping and is similar to the doping of silicon and germanium that made transistors possible.

1.3.1.2 Polymer Composites

Composites are considered to be combinations of materials differing in composition or form on a macro scale. The constituents retain their identities in the composite; that is, they do not dissolve or otherwise merge completely into each other although they act in concert. Normally, the components can be physically identified and exhibit an interface between one another. Nature uses composites for all her hard materials. These are complex structures consisting of continuous or discontinuous fibrous or particulate material embedded in an organic matrix acting as glue. Wood is a composite of fibrous cellulose and lignin. Bone is a composite of collagen and other proteins and calcium phosphate salts.

Polymer composites could be characterized broadly as two phase materials: a primary polymeric continuous phase and a secondary or dispersed phase generally referred to as matrix and filler phases, respectively. Thus these materials contain an
electrically insulating polymer matrix loaded with a conductive filler. The addition of fillers to polymers allows us to envisage the elaboration of polymers possessing the conductive properties of metals and the varied properties of polymers. Conductive polymers have many advantages over metallic conductors. They can be easily shaped with low cost; they have light weight; they provide corrosion resistance and they can offer a wide range of electrical conductivities. The addition of fillers markedly increases the conductivity of typical polymeric insulators. The volume resistivity of insulators often ranges from $10^{12}$ to $10^{18}$ ohm-cm. Mechanisms of conduction include tunnelling, ionic transport, electron hopping, dielectric breakdown, field emission and simple interaggregate conduction. As the concentration of the filler increases, the mode of conduction changes from tunnelling to direct conduction \[7\]. The most important polymers that can be used as matrices are: polyethylene, polyamides, polyesters, poly vinyl chloride (PVC), poly vinyl acetate (PVAc), polyurethane, poly vinyl alcohol (PVA), styrene acrylonitrile (SAN), acrylonitrile butadiene styrene (ABS), and acrylcs e.g. polymethyl methacrylate (PMMA), etc. The often used conductive filler materials include, metal powders (i.e., Al, Au, Ag, Cu, Pd, Pt and stainless steel), carbon black (CB) or graphite powders \[9-11\] and semiconducting metal oxides ($V_2O_3$, $V_2O_5$, TiO$_2$ etc.). Contrary to the carbon black/graphite particles, the powdered metal particles do not usually aggreate or agglomerate \[12\]. Different conductivity ranges\[13-17\] can be achieved by adding a suitable filler into the polymer matrix. Fillers can also affect other properties such as hardness, elasticity, colour besides conductivity. In other words certain fillers are more appropriate than others for functioning in special applications. Generally the conductivity of such mixtures increases drastically at a certain concentration of the conductive component, the so-called percolation concentration. Among the parameters influencing the
percolation concentration, the filler distribution, filler geometry (size & shape), filler/matrix interactions and the processing technique are the most important ones [18-19]. There is a myriad of filler element geometries possible e.g. spherical, cylindrical, in the form of fiber or flakes etc.

1.4. Percolation Threshold

Electrical resistivity is generally not much affected by the addition of conducting filler until a critical composition is reached when an infinite filler particle-particle contact chain first appears in the system, resulting in a dramatic fall in electrical resistivity. A critical concentration of the filler, beyond which the polymer composite becomes electrically conductive, is referred to as the percolation threshold. This critical weight or volume fraction is called the percolation concentration. In other words, percolation threshold may be defined as the lowest concentration of conducting filler particles at which continuous conducting chains or branching is formed. At this point a conductive network of channels is formed within the matrix, which permits the movement of charge carriers of the fillers through the matrix, and so the composite achieves a certain degree of electrical conductivity [22-23]. As the filler concentration is increased beyond this critical composition, the fraction of particles in the infinite chain increases till a second critical point where complete filler particle contacts are established throughout the matrix. Beyond this, a further increase in filler concentration does not affect the electrical resistivity appreciably [24]. The concept of percolation can be used to understand the change in resistivity as a function of filler concentration in composites. It describes the conduction with the presence of electrically conducting paths between two filler particles. The number of
these conducting paths will be dramatically destroyed below the critical volume fraction of the filler.

The conductivity of the composite is related directly to the conductivity of the filler, the matrix and the quality of the electrical network formed. Percolation occurs when there are enough particles for a consistent electrical network to be formed by physical contact or tunnelling of electrons through thin layers of matrix separating the inclusions [25]. While large excess of conductive particles provide enough surface and volume conductivities, mechanical strengths deteriorate because of the presence of large fractions of particles in the polymer matrix. Consequently, the amount of conductive particles must be decided from a balance of mechanical performance and desired level of conductivity [26]. Since higher filler levels tend to change mechanical properties, the most versatile composite has a filler level just above the percolation point. One of the main areas of technological interest in the field of polymer composites is thus the enhancement of electrical conductivity with a low concentration of conducting fillers. [27-30].

Changes in the conductivity of the polymers on the addition of conductive fillers have been interpreted in terms of percolation theory [8]. To understand the network formation on a scientific level, many so-called percolation models and equations have appeared in the literature [31-45]. On the basis of filler and polymer properties and the processing parameters for the fabrication of composites, different models have been proposed aimed at the prediction of the conductivity both below and above the percolation concentration. Some of the most important percolation models are discussed in chapter III.
1.5 Random and segregated distributions

There are essentially two types of distributions of the filler particles in the polymer matrix: random and segregated [46-47]. The former refers to the comparable particle size of the polymer and the filler whereas the later occurs when the polymer particles are relatively larger in size than the filler particles. Coler [48] first reported the use of fine powders especially copper and silicon, to make acrylics, vinyls and polysterene conductive with a resistivity of the order of 0.01 to 0.1 ohm-cm through the formation of a “reticulate structure” later termed as “segregated network” by Malliaris and Turner [49]. When mixtures of particles of polymer and filler are compacted the filler does not penetrate the polymer and consequently it is possible to make samples with a segregated distribution of the filler.

Segregation is achieved initially through the tendency of the small particles of the filler ($R_f$) to adhere on to the relatively much larger particles of the polymer ($R_p$) where $R_f$ and $R_p$ represent the filler and polymer particle average radii respectively. Figure 1.1 illustrates the formation of segregated networks in composites by compacting mixture under heat and pressure. The deformation of polymer particles due to elevated temperature and pressure is also demonstrated in the diagram. It has been observed that the segregated distribution of the conductive filler phase in a polymer matrix leads to the formation of a conductive network at a rather low critical concentration of conductive filler. Figure 1.2 shows the resistivity of Lupolen-Z/MT black composite as a function of filler concentration for both random and segregated distributions [52]. This figure clearly exhibits the onset of percolation at low carbon loadings in case of segregated distribution. Randomly dispersed particles will not form a network until their volume concentration reaches 40%. At such high loadings,
however, the material loses the advantage of being a tough plastic. Instead, it becomes a relatively weak, brittle structure.

Figure 1.1 Illustration for the formation of segregated conducting networks. The big White circles represent polymer particles of radius $R_p$ and black smaller circles represent filler particles of radius $R_f$ [49].
The method to attain segregated distribution of the conducting filler phase is based on prolonged tumble mixing of a dry-blended mixture consisting of a conductive filler and polymer powder which results in the coating of filler particles onto the surface of polymer particles. The mixture is then compressed and molded. This process is referred as pre-localization of the conductive phase. The conductive filler particles remain essentially located at the interface between polymer particles building up a continuous conductive network of channels [48]. It has been discovered that the filler can be localized at the interfacial boundary between two phases of an immiscible polymer blend when it is mixed with filler in melt [50-51]. This method has been adopted for the fabrication of composites in the present study, to ensure segregated distribution. The percolation concentration decreases as the ratio \( R_p / R_f \) increases.

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Figure 1.2  Resistivity of Lupolen Z- MT Black composite as a function of filler distribution and concentration.
1.6 Applications of conducting polymer composites.

The design of electroconductive polymer composites with low percolation threshold for a variety of applications has added new dimension to scientific interest in the last couple of decades. Applications of electroconductive polymer composites [53-63] in the area of electrical and electronic field are significant for the modern technology. Advances in high-speed electronics miniaturization have stimulated demands for cost effective, conductive materials for circuit components and screens [64]. Conducting polymers offer many advantages over classic materials (metal, wood etc.) such as easier processing, cost effectiveness, lesser density compared to metals, preservation from corrosion and varied mechanical properties (strength, flexibility and environmental resistance). As these conductive polymers retain some of the advantages of conventional polymers, such as density, cost and processibility they present tremendous potential as an alternate to metals for specific purposes and widen the range of applications. These materials have variety of applications such as electromagnetic/radio frequency interference shielding in electronic devices e.g. plastic housings of computers and cellular phones, temperature and current sensor devices [21], current limiting devices in circuit protection [65-69], antistatic materials (antistatic agents are chemicals which provide a conductive coating on a polymer surface so that static charges can be leaked off), self-regulating heaters etc [70,71].

1.6.1 EMI Shielding

Polymers contain a very low concentration of free charge carriers, and thus they are non conductive and transparent to electromagnetic radiation. Due to this reason these materials are not suitable for being used as enclosures for electronic
equipment as they cannot shield it from outside radiation or prevent the escape of radiation from the component. They also cannot provide protection against electrostatic discharge in handling sensitive electronic devices. A single cellular device transmits and receives several types of information, such as voice, text, and video. The integration of high-speed, broadband digital and analog transmissions is the need of present cellular communication systems. In such heterogeneous traffic systems of communication, the controlling of electromagnetic interference (EMI) is highly essential. These requirements led to the growth in research for electrically conductive polymers. Plastic housing of cellular phones and computers with a controlled EMI has thus become a reality today!

1.6.2 Sensors

Sensors play a vital role in almost all aspects of contemporary society. The field of sensors has made an indelible impact on all aspects of modern day life. Whether it is industrial or domestic, agricultural or biomedical, automobile or space, defence or security, computers or robotics, medical or scientific research, sensors have made their presence felt in almost every field. As a matter of fact the sophistication of a system can be judged by the quality and technology of the sensors used to fabricate it. Some times new applications are sought and use of a particular sensor is justified by its special features. No measurement, control and navigation function can be carried out without sensing the variable parameters involved. A sensor can be defined as a device that gives signal for detection/measurent of a physical or chemical parameter to which it responds. These are used to measure physical parameters such as, pressure, temperature, acceleration, light, stress etc. and chemical parameters such as vapour pressure, humidity, medical and biomedical parameters such as blood pressure, blood sugar etc. Presently computer controlled
systems continually monitor the operating conditions of existing machines and devices. Through sensors computers receive vital information about a number of conditions, allowing minor adjustments to be made far more quickly and accurately than mechanical systems. Sensors convert temperature, pressure, speed, position and other data into either digital or analog electrical signals. The computer uses the sensor data to control different systems in a device through the use of actuators. An actuator is an electromechanical device such as a relay, solenoid or motor.

Though the physical principle may be same, but the use of new materials and technology adds certain new features to the sensor. Polymeric materials have gained a wide theoretical interest and practical application in the field of sensors. They can be used for very different purposes and may offer unique possibilities. They offer a lot of advantages for sensor technologies: they are relatively low cost materials, their fabrication techniques are quite simple, there is no need for special clean room and/or high temperature processes, they can be deposited on various types of substrates. The wide choice of their molecular structure and the possibility to build in side-chains enables composites to be produced with various physical and chemical properties including the sensing behaviour. Active sensing polymers are used in bulk as well as film forms as an integral part of solid-state devices.

The design of electroconductive polymer composites as an intelligent material [21,72,73] that can perform both sensing and actuating function is an important milestone in the field of sensor technology. All the environmental effects that can change the volume fraction of the filler, such as temperature because of a mis-match between the coefficient of expansion of the filler and the polymer, deformation due to the elasticity coefficient differences, and polymer swelling due to the absorption of vapour or humidity, may cause a change in resistivity [74]. These materials are
capable of sensing a change in the environment and respond to it in a technical way. The important physical parameters to be sensed are the temperature, pressure, electrical current, electric field and vibration and the useful responses are heating, cooling, change in electrical resistance and acoustic or mechanical damping. A number of such technically smart materials with such responses have already been proposed [59-62]. The sensitive dependence of conductivity on temperature of polymers loaded with conductive fillers can therefore be used in the design and fabrication of electrical switching devices.

When the resistance of a material increases with the increase in temperature, the effect is known as positive temperature coefficient of resistance (PTCR) [75-78]. All materials with metal-like conduction exhibit a PTCR phenomenon. The resistivity of metals generally falls in the range of 1-100 $\mu\Omega$-cm. In these materials, the PTCR effect is characterized by increase in resistance linearly with temperature. This is the normal PTCR effect.

Some heterogeneous mixture of materials may exhibit a resistance that increases sharply over a narrow temperature range. Certain types of conductive polymers exhibit this effect. These polymers are useful for making over-current protection devices, generally called polymeric PTCR over-current limiters, circuit protection devices, or resettable fuses.

1.6.2.1 Current limiters

Electroconductive polymer composites normally exhibit PTCR effect. As the temperature increases, the plastic material will expand more than the conductive filler, which will increase the distance between the conductive particles. Therefore, the potential barrier (gap) increases and resistivity increases. This is the basis of forming the PTCR phenomenon in polymer composites. The distinguishing characteristic of
all PTCR composites is an abrupt increase in electrical resistance within a narrow, distinct temperature range. The transition of a polymer composite from lower resistivity state to high resistivity state can be utilized for making current limiters for electric circuits. The unique resistance switching property of these materials forms the basis for their use as current limiting devices in electrical and electronic circuits. In overload conditions, the joule heating due to the excess current causes the material temperature to rise above the PTCR transition temperature, thereby compelling the material to switch to its high resistance state. In this state, the overload current is limited to an acceptable value. When the overload condition is cleared, the device cools below its switch temperature and normal circuit operation is resumed. Such limiters are presently being used for the protection of electric and electronic components in circuit boards for controlling currents ranging from fraction of an ampere to several amperes [80]. They are used in low voltage distribution systems at ratings upto 63 amperes.

1.6.2.2 Self-temperature control heaters

Self-temperature control heaters also work on a similar principle. The function of self-temperature control in conducting polymer composite heaters arises from an abrupt increase in resistance at a characteristic temperature. Let us assume that electrical power is supplied to such a heater. If it overheats, the resistance increases, the power dissipated (under a constant voltage condition) drops precipitously and the sample cools down. If it overcools, the resistance decreases and the power dissipated increases and so on. This is the common behaviour of the self-temperature control heaters known at present. This behaviour has been explained in terms of the volume expansion of the matrix due to rise in temperature [81].
1.7 Materials used in the present study

Materials for the present work have been chosen on the basis of their commercial availability, cost effectiveness and their widespread use. The two polymers, acrylonitrile butadiene styrene and poly vinyl chloride are commonly used in a number of applications including fabrication of conductive polymer composites. Data is available in the literature for comparing results.

Among the many requirements for an ideal filler for polymer modification, a few important characteristics listed by King [79] are: maximum improvement of the desired physical properties, low moisture absorption, specific gravity appropriate for the application, freedom from deleterious chemical impurities and objectionable physical effects, low cost and good availability, non-inflammability, odourlessness, good colour, good chemical resistance, good heat resistance, availability in controlled particle sizes, good dispersion characteristics and low solubility in water and environmental solvents.

No single known material could meet all the requirements necessary for potential filler. The choice of filler plays a very vital role in polymer modification as the properties and proportions of the component materials control the final properties of the composites. A large number of variables viz. size, shape, nature, state of distribution of the filler, adhesion and thermal compatibility of the filler etc. characterize the system and some of them have strong influence on the properties of the composites. Bigg [20-21] has reviewed the development of electrical properties of metal filled polymers and the mechanism involved in the formation of conductive composites of polymer/metal systems. The advantage of metallic powders over other fillers is that they introduce good electrical and thermal conductivity into the
composite. These fillers, however, generally suffer from the oxidation of the metallic particles and the corresponding deterioration of the electrical properties of the composite due to the nonconductive nature of such oxide layers. Another disadvantage of the metallic fillers is relatively higher density of metals (copper- 8.9 gm/cm$^3$, silver- 10.3 gm/cm$^3$) in comparison to polymers due to which the metallic powder tends to settle at the bottom of the tumbler during mixing creating a hindrance in achieving homogeneity. Thus graphite, a relatively cheaper material than metals, having density 1.75 g/cm$^3$ and conductivity 1.33x10$^4$ S/cm has been selected as filler for the present study. To achieve thermal conductivity additives like graphite, carbon fibers, and ceramics like Aluminum Nitride or Boron Nitrides are used. Graphite provides electrical as well as thermal conductivity while ceramics provide only thermal conductivity.

1.7.1 Polyvinyl chloride (PVC)

Polyvinyl chloride was accidentally discovered on at least two occasions in the 19th century, first in 1838 by Henri Victor Regnault and in 1872 by Eugen Baumann. Polyvinyl chloride is a major thermoplastic material finding use in a very wide variety of applications and products. The essential raw materials for PVC are derived from salt and oil. The electrolysis of salt-water produces chlorine, which is combined with ethylene, obtained from oil, to form vinyl chloride monomer (VCM). Molecules of VCM are polymerized to form PVC resin, to which appropriate additives are incorporated to make a customised PVC compound. PVC is polymerized from its monomer, vinyl chloride (chemical formula CH$_2$ = CHCl) as illustrated in equation 1.1.


Vinyl chloride monomer  Polyvinyl chloride polymer

PVC is a hard plastic that is made softer and more flexible by the addition of plasticizers, the most widely used being phthalates. PVC’s major benefit is its compatibility with many different kinds of additives, making it a highly versatile polymer. PVC can be plasticised to make it flexible for use in flooring and medical products. Its compatibility with additives allows for the possible addition of flame-retardants although PVC is intrinsically fire retardant because of the presence of chlorine in the polymer matrix. PVC has excellent electrical insulation properties, making it ideal for cabling applications. Its good impact strength and weatherproof attributes make it ideal for construction products. Clear or coloured, rigid or flexible, formulation of the compound is key to PVC’s "added value". There are many uses for PVC including vinyl siding, window profiles, gramophone records (hence the ones made of this material are sometimes called vinyl records) and pipe/plumbing/conduit fixtures. In its soft form it is used for clothing, upholstery (car seats), flooring, roofing membranes, electrical cables etc.

1.7.2 Acrylonitrile-Butadiene-Styrene (ABS)

Styrene Acrylonitrile copolymer has been available since 1940’s and while its increased toughness over styrene made it suitable for many applications, its limitations led to the introduction of a rubber (butadiene) as a third monomer and hence was born the range of materials popularly referred to as ABS plastics. These became available in 1950’s and the variability of these copolymers and ease of
processing has led to ABS becoming the most popular of the engineering polymers. ABS is a copolymer of acrylonitrile, butadiene, and styrene. ABS is one of the most common polymer materials. It is a two-phase polymer blend. Styrene and Acrylonitrile form a linear copolymer (SAN) that serves as a matrix. Butadiene and Styrene also form a linear copolymer popularly known as BS rubber.

The combination of the two copolymers gives ABS an excellent combination of strength, rigidity, and toughness. ABS is often used as the cost and performance dividing line between standard plastics (PVC, polyethylene, polystyrene, etc.) and engineering plastics (acrylic, nylon, acetal, etc.). ABS can be given a range of properties, depending on the ratio of the monomeric constituents and the molecular level connectivity. ABS has good chemical resistance to inorganic salt solutions, alkalis, mineral acids (except strong oxidizing acids), and some mineral, vegetable, and animal oils. ABS is also one of the few non-metallic materials, which can be readily electroplated. The natural ABS is opaque, having ivory colour and can be readily coloured with pigments or dyes. Transparent grades are also available. ABS is an ideal material wherever superlative surface quality; colourfastness and luster are required. The chemical formula of ABS is:

```
. —-CH2 - CH - CH2 - CH = CH - CH2 - CH2 - CH -
    |     |     |     |
    CN   |     |
```

25
ABS has a very wide range of applications because of its good balance of properties like toughness/strength/temperature resistance coupled with its ease of molding and high quality surface finish. These include, telephone handsets, computer and other office equipment housings, lawn mower covers, cassette holders, business machine housings and trays, water purification equipment, laboratory equipment, household fixtures, safety helmets, luggage shells, pipes and fittings etc.

<table>
<thead>
<tr>
<th>Table 1.1 Properties of PVC and ABS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Property</strong></td>
</tr>
<tr>
<td>Colour</td>
</tr>
<tr>
<td>Density</td>
</tr>
<tr>
<td>Melt Flow</td>
</tr>
<tr>
<td>Hardness, Shore D</td>
</tr>
<tr>
<td>Electrical Resistivity (at Room Temperature, R.T.)</td>
</tr>
<tr>
<td>Dielectric Constant (at 100KHz, R.T.)</td>
</tr>
<tr>
<td>Dissipation Factor (at 100KHz, R.T.)</td>
</tr>
<tr>
<td>Linear coefficient of expansion (at R.T.)</td>
</tr>
<tr>
<td>Glass Temperature</td>
</tr>
</tbody>
</table>

Because of the availability of electroplatable grades, ABS is often found as automotive/ aircraft interior and exterior components. Electrical and electronics industries increasingly require surfaces, which are not only highly scratch- and wear-
resistant but also decorative and easy to maintain. Its excellent antistatic performance is a particular advantage here. The major applications for thermally conductive plastics would be in microelectronics to provide the desired heat sinks to pack more in smaller space. In the present study its use as a temperature and current sensing material by adding conducting filler into it has been investigated. Newer applications will emerge once their costs are lowered. The various properties of PVC and ABS are listed in Table 1.1.

1.7.3 Carbon/Graphite

Carbon, the sixth most abundant element in the universe, has been known since ancient times. It is one of the most versatile chemical elements, which forms the backbone of almost all molecules important to life, such as DNA, proteins and oils. The unique character of carbon stems from the ability of its atoms to form stable bonds among themselves, while most other elements prefer different partners in chemical bonds. Carbon is commonly obtained from coal deposits, although it usually must be processed into a form suitable for commercial use. Since the late eighties, there were only two known forms of pure crystalline carbon: diamond and graphite. In diamond every atom is surrounded by four other carbons, forming a three-dimensional network, whereas in graphite every carbon binds with three neighbouring atoms in a plane, leading to a chicken wire like sheet (Fig. 1.3). These graphite sheets are loosely coupled with one another and slide easily, giving it a soft texture. In addition to bulk graphite and diamond, carbon materials are found in a variety of forms such as carbon black of various origins, carbon fibers and carbon nanotubes. These various forms of carbon may be quite different with regard to structure and properties. Carbon fibers and carbon black and graphite are widely used in industry as fillers to improve the
mechanical, electrical and optical properties of the matrix in which they are dispersed.

Graphite, one of the softest materials known, is a form of carbon that is primarily used as a lubricant. Although it does occur naturally, most commercial graphite is produced by treating petroleum coke, a black tar residue remaining after the refinement of crude oil, in an oxygen-free oven. Naturally occurring graphite occurs in two forms, alpha and beta. These two forms have identical physical properties but different crystal structures. All artificially produced graphite is of the alpha type. In addition to its use as a lubricant, graphite, in a form known as coke, is used in large amounts in the production of steel. Coke is made by heating soft coal in an oven without allowing oxygen to mix with it.

Diamond, the second naturally occurring form of carbon, is one of the hardest substances known. Although naturally occurring diamond is typically used for jewellery, most commercial quality diamonds are artificially produced. These small diamonds are made by squeezing graphite under high temperatures and pressures for several days or weeks and are primarily used to make things like diamond tipped saw blades. Although, graphite and diamond differ only in their crystal structure they exhibit very different physical properties.

There are nearly ten million known carbon compounds and an entire branch of chemistry, known as organic chemistry, is devoted to their study. Many carbon compounds are essential for life, as we know it. Common carbon compounds are: carbon dioxide (CO₂), carbon monoxide (CO), carbon disulfide (CS₂), chloroform (CHCl₃), carbon tetrachloride (CCl₄), methane (CH₄), ethylene (C₂H₄), acetylene (C₂H₂), benzene (C₆H₆), ethyl alcohol (C₂H₅OH) and acetic acid (CH₃COOH). A soft, steel-gray to black, hexagonally crystallized allotrope of carbon with a metallic luster
and a greasy feel, used in lead pencils, lubricants, paints, and coatings, graphite is fabricated into a variety of forms such as powder, molds, bricks, electrodes, crucibles, and rocket nozzles.

An allotropic form of carbon, also known as plumbago and black lead, crystalline (often in the form of slippery scales), greasy, and soft material with a metallic luster, graphite is a good conductor of electricity and does not fuse even at very high temperatures or burn easily. It occurs in nature in grayish-black masses, massive or crystalline. It is also prepared artificially by treating hard coal in the electric furnace, a process discovered by E. G. Acheson.

The basic structure of graphite depicted in figure 1.3 consists of a hexagonal arrangement of carbon atoms which form stable planar lattices with only weak interlayer bonding (Van-der Waals forces). These lattices are individually very rigid but each is able to slide easily over adjacent layers. This crystal structure is the principal reason for the unique properties of graphite which result in their inherent suitability as raw materials for a wide variety of applications. Associated minerals include: quartz, calcite, mica and tourmalines. These are generally found in the USA, Russia, Mexico, Greenland, Sri Lanka and India.

The unit cell dimensions are \( a = b = 245.6 \) picometres (pm), \( c = 669.4 \) pm. The carbon-carbon bond length in the bulk form is 141.8 pm, and the interlayer spacing is \( c/2 = 334.7 \) pm. Each carbon atom possesses an sp\(^2\) orbital hybridisation. The pi orbital electrons delocalized across the hexagonal atomic sheets of carbon contribute the graphite's conductivity. In an oriented piece of graphite, conductivity parallel to these sheets is greater than that perpendicular to these sheets.

The thermal properties of graphite are also highly anisotropic; phonons propagate very quickly along the tightly bound planes, but are slower to travel from
one plane to another. The loose coupling among the sheets in graphite contributes to another industrially important property -- graphite powder is used as a dry lubricant. Recent studies suggest that an effect called superlubricity can also account for this effect.

Fig. 1.3 Crystal Structure of Graphite
Table 1.2 properties of Graphite

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>gm/cm³</td>
<td>1.75</td>
</tr>
<tr>
<td>Particle size</td>
<td>µm</td>
<td>10-20</td>
</tr>
<tr>
<td>Colour</td>
<td></td>
<td>black</td>
</tr>
<tr>
<td>Modulus of Elasticity (Young’s Modulus)</td>
<td>GPa</td>
<td>4.8</td>
</tr>
<tr>
<td>Max. Use Temperature (inert atmosphere)</td>
<td>°C</td>
<td>3600</td>
</tr>
<tr>
<td>Electrical Resistivity (at R.T.)</td>
<td>Ohm·cm</td>
<td>7.5 x10⁻⁵</td>
</tr>
</tbody>
</table>

The uses of graphite are wide and diverse. The so-called lead of pencils is in reality a mixture of graphite with clay. Crucibles required to withstand high temperatures and also electrodes are commonly made of graphite. Unlike diamond, graphite is a conductor, and can be used, for instance, as the material in the electrodes of an electrical arc lamp or as conducting filler in the preparation of polymer composites. The various properties of graphite are listed in Table 1.3.

1.8 Objective of the thesis

The original impetus of this work is the fabrication of polymer composites with low room temperature resistivity at smaller filler loadings and the study of the effect of temperature on the resistivity of these composites. Analysis of the data in terms of few existing conductivity models in order to examine the authenticity of these models has also been carried out. The effect of percolation threshold on electrical, dielectric and mechanical properties has also been studied. The study of the relationship between the temperature and resistance of the conducting polymer
composites is especially carried out for finding novel sensor materials. The approach involved the selection of an appropriate type of conductive filler, tailoring the particle shape and size distribution, the optimization of the filler concentration and the selection of a suitable processing technique. The volume loading levels, which are relevant to the percolation regime of the composites, at which the composite changes from an insulator to a conductor, are especially focused upon.

Electrically conductive polymer composites are fabricated using indigenously available materials i.e. natural flake graphite as conducting filler and two electrically non-conducting polymers viz. poly vinyl chloride (PVC) and acrylonitrile butadiene styrene (ABS). Graphite (10-20 micron) powder and powder of polymer were tumble-mixed thoroughly for long time to ensure homogeneity in mixing. The dry blended mixture of powders of polymer and graphite so obtained is compressed and molded below the glass transition temperature to attain segregated distribution. The conductive filler particles will thus remain located at the interfacial regions between the polymer particles and build up a three-dimensional network of conductive pathways.

In conductive pathways actual physical contact between neighbouring particles need not to be present, but they should at least be within the close proximity for electron to jump/ tunnel. The dimension of channels is directly related with filler concentration. As the filler concentration approaches the percolation threshold, the sharp decrease in the resistivity is due to the combined effect of an increase in dimension of conductive channels and a decrease in the interparticle distances. For composition higher than that of a critical filler fraction, many conductive continuous chains of filler particles co-exist with some nonconductive deadlock branches.
The investigations such as Differential Scanning Calorimetry (DSC) for and Scanning Electron Microscopy (SEM) have been carried out for finding glass transition temperature Tg and for studying morphology respectively. Investigations of I-V characteristics as a function of filler content for various processing conditions ascertain the transport mechanism in polymer composites. The study of variation of specific resistivity as a function of temperature for different filler content is essential in order to observe any sharp increase of resistivity in a small and well-defined range of temperature for sensor application. Since filler loading in composites influences room temperature resistance and intensity of positive temperature coefficient (PTC), such studies become most important in relation to the present perspective. As the mechanism to explain the electrical phenomena, which involve percolation, PTCR and negative temperature coefficient of resistance (NTCR), is still controversial, a better understanding is essentially required. The investigations will give a better and clear understanding of mechanism of electrical phenomena. Although electrical conductivity of the polymer composites has been studied by many researchers and there is a plethora of research papers in the literature, the dielectric properties has rarely been addressed to. In the present study the dielectric behaviour (dielectric constant, loss factor and dissipation factor) of the prepared composites vis-à-vis the filler concentration and the frequency of the measuring electric field are also investigated.

The studies of D Shore Hardness versus filler concentration are carried out to understand as to what extent the mechanical strength of the polymer is scarified due to the addition of the conducting filler.
1.9 Brief Outline of the Thesis

The results of present investigation along with the necessary theoretical and experimental details are given in this thesis. The thesis is divided into six chapters. The chapter wise break-up is given below:

Chapter I General Introduction

This chapter provides a brief overview of the polymer composites in the context of the topic of the thesis. In the beginning a brief description of the general properties of the polymers and the distinction between amorphous and crystalline/semi crystalline polymers is given. It is followed by the classification of conducting polymers. Brief introduction to the percolation threshold i.e. a critical concentration of filler beyond which the composite becomes electrically conductive is given. Two types of distribution of the filler in the polymer i.e. random and segregated are then explained. Applications of the polymer composites in the field of EMI shielding in general and in the field of temperature sensors in particular are described. Finally a brief description of the properties of the materials used in the preparation of the composites for this study is given.

Chapter II Experimental

The various methods for the fabrication of conducting polymer composites by adding conducting fillers are briefly given in the beginning of this chapter. This is followed by the details of the technique used for the preparation of the samples for the present study i.e. the hot compression molding with pre-localization of the conductive phase. The whole process of fabrication of the samples is explained with the help of a flow chart. The values of various processing parameters i.e. the pressure, temperature and the time are then given. This is followed by the method of resistance
measurement as a function of filler volume fraction and temperature. The method of studying the variation of current with voltage is then described. A brief introduction regarding the determination of dielectric properties is also provided. Finally the characterization techniques used in the present study i.e. the D Shore Hardness and the microstructure determination using SEM are described.

Chapter III Percolation Models

The objective of this chapter is to give a general introduction to the percolation theory and models. Percolation theory is based on the idea that a large change of properties will occur when the second phase (filler) is totally connected from one side of the composite to the other. The volume fraction at which this occurs is called the percolation threshold. In the beginning a brief discussion of the explanation of the percolation theory as described by various researchers in the literature is given. Factors affecting the electrical conductivity of the composites on addition of the filler are also discussed. The electrical conductivity models, which are relevant to the carbon black/graphite filled composites i.e. the statistical model and the thermodynamic modes are then described. Finally the data obtained in respect of the PVC/Gr and ABS/Gr polymer composite in this study is examined in the light of the statistical models.

Chapter IV Effect of percolation on Electrical, Dielectric and Mechanical Properties of Composites

This chapter deals with the effects of the percolation threshold on the electric, dielectric and mechanical properties of the fabricated composites. Firstly the variation of current with voltage for different concentrations of the filler, both below and above the percolation threshold is reported for both PVC/Gr and ABS/Gr composite
systems. From the logV-logI plots the quantitative change in the non-ohmic behaviour of the I-V characteristics with graphite concentration is evaluated and a comparison between the two systems has been made. Secondly the dielectric properties i.e. the relative permittivity, the loss factor and the dissipation factor are determined by performing several isothermal scans as a function of frequency and composition in order to examine changes near the percolation threshold concentration. The behaviour of the composites in respect of the dielectric properties is explained on the basis of interfacial Maxwell Wagner polarization for heterogeneous systems. The ac conductivity of the composites is calculated from the dielectric data and its variation with the composition and frequency is studied. Finally the change in the D Shore Hardness and the microstructure of the composites as a function of graphite concentration is reported.

Chapter V Effect of temperature on the Resistivity of composites

This chapter describes the effect of change in temperature on the resistance of the PVC/Gr and ABS/Gr composite systems. As the endeavor of this study is to develop and characterize polymer composite material suitable for sensors, a thorough investigation of any appreciable change in resistance of the composite within a small narrow temperature range is indispensable. Thus the two composite systems were tested for this property and the findings are provided in this chapter. The reproducibility of changes over a number of repeated temperature cycles in case of ABS/Gr composite has also been reported. Finally a theoretical explanation for the change in resistance near the glass transition temperature is given and a mathematical analysis as to how a material having a non-linear PTC can be used as a switching device is also provided.
Chapter VI Conclusions

In this chapter the various conclusions that are drawn from the present studies are incorporated. The percolation threshold has been achieved at low value of the filler concentrations. This ensures the fabrication of polymer composites without compromising their mechanical strength. The conductivity data obtained experimentally was found to be in good agreement with the Power Law Model. The standard mixing rules however failed to predict the conductivity of the composites. The study of dielectric properties as a function of frequency and composition establishes the importance of taking into account the frequency dependence while dealing with the conducting polymer composites. This bears more relevance when the volume fraction of the filler is in the vicinity of percolation concentration. The study of the effect of temperature on resistivity reveals that in case of PVC/Gr composite the increase in resistivity with temperature is gradual and the reproducibility is poor. In case of ABS/Gr composite, however a sharp increase in the resistivity in the vicinity of glass transition temperature is observed. This effect is most pronounced in case of composite having filler fraction near percolation threshold. This system also exhibited a good reproducibility under repeated heating and cooling although a slight increase in the room temperature resistivity is observed after each heating/cooling cycle. This property makes ABS/Gr composite a potential candidate for fabricating current and temperature sensing devices.
1.10 References


76. E. Frydman, UK Pat. Spec. 604695, 8 July 1948.